unit

7 Electrochemistry

Figure 1
Dr. Viola Birss

You have previously classified chemical reactions using empirical generalizations such as single replacement. This classification of reactions is useful because it helps you to make predictions that generally can be verified in a laboratory. However, these predictions do not require any theoretical knowledge about how the reaction actually occurs. Chemists classify most common reactions based on a theoretical understanding of the reaction process. One very important example is the electron–transfer reaction, known as an electrochemical reaction. The study of chemical reactions associated with the transfer of electrons is known as electrochemistry.

Electrochemical reactions may be the most important reactions on Earth. Living things use electrochemical reactions for photosynthesis and metabolism. Nonliving things undergo electrochemical reactions such as corrosion, (as shown by the metal door in the photograph), metallurgy, and combustion.

Electrochemistry can be applied to solve various technological problems. For example, the research conducted by Dr. Birss (**Figure 1**) and her research team at the University of Calgary is rooted in electrochemistry. According to Dr. Birss, "One of the main goals of our research over the last 15 years has been to produce useful thin film materials that can serve as electrocatalysts in fuel cells, to protect metals from corrosion, as a matrix for enzymes for biosensor applications, and to create useful nanoarchitectures."

Research into fuel cells involves developing new catalysts of nanometre-sized metal or metal oxide particles, researching new low-cost cathode materials for the reduction of oxygen in fuel cells, and investigating factors that affect the performance of these cells. Dr. Birss' team is also researching the development of novel electrochemical methods of coating metals with protective oxide films, which is of particular interest to the aerospace and oil and gas industries, and the development of glucose biosensors for people with diabetes.

As you progress through the unit, think about these focusing questions:

- What is an electrochemical change?
- How have scientific knowledge and technological innovation been integrated in the field of electrochemistry?

NEL

GENERAL OUTCOMES

In this unit, you will

- explain the nature of oxidation–reduction reactions
- apply the principles of oxidation–reduction to electrochemical cells

ARE YOU READY?

These questions will help you find out what you already know, and what you need to review, before you continue with this unit.

Prerequisites

Concepts

- atoms and ions
- ionic and covalent bonding
- balanced chemical reaction equations
- dissociation and ionization
- mole concept and stoichiometry

Skills

- safe handling and disposal based on WHMIS
- diagnostic tests
- solution preparation
- reaction equipment and procedures
- chemical amount and stoichiometry calculations
- designing and evaluating experiments
- SI and IUPAC communication conventions

You can review prerequisite concepts and skills in the Chemistry Review unit, on the Nelson Web site, and in the Appendices.

A Unit Pre-Test is also available online.

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Knowledge

1. When a metal atom forms an ion, the atom _____ electrons to form a _____ charged ion.
2. When a nonmetal atom forms an ion, the atom _____ electrons to form a _____ charged ion.
3. According to trends in the periodic table and your general chemistry knowledge, copy and complete **Table 1**.

Table 1 Reactivity of Elements

Category	Groups or examples
most reactive metals	
least reactive metals	
most reactive nonmetals	
least reactive nonmetals	

4. Complete the following chemical equations using Lewis symbols or formulas for the products.

(a) $K\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow$
potassium + chlorine $\rightarrow$

(b) $\cdot\ddot{\underset{\cdot}{P}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow$
phosphorus + chlorine $\rightarrow$

(c) Compare electron rearrangement in (a) to electron rearrangement in (b).
(d) According to the bonding theory you have studied, what is believed to determine whether two atoms transfer or share electrons?

5. (a) Write the generalized chemical equation for a single replacement reaction.
(b) How do you know what class of element—metal or nonmetal—forms in a single replacement reaction?

6. Complete and balance the chemical equation for each of the following reactions:
(a) $__\ Zn(s) + __\ AgNO_3(aq) \rightarrow$
(b) $__\ Cl_2(aq) + __\ KBr(aq) \rightarrow$
(c) $__\ Al(s) + __\ HCl(aq) \rightarrow$
(d) $__\ C_3H_8(g) + __\ O_2(g) \rightarrow __\ CO_2(g) + __$

STS Connections

7. When lead ion solutions are used in a laboratory, disposal of reactant solutions and products requires special care. The recommended method for lead disposal is to precipitate all lead(II) ions in the form of the insoluble lead(II) silicate. This solid can then be disposed of as regular solid waste as long as it is buried and not incinerated.
(a) Why should lead compounds not be incinerated or disposed in a soluble form down the drain?

(b) Briefly describe the issue related to lead in the environment. What was the most common source of lead pollution until legislation forced a change in the substance sold?
(c) Suggest a reason why it is acceptable to bury a lead compound that is not soluble in water.
(d) When excess sodium silicate solution was added to 150 mL of lead(II) nitrate solution, 2.41 g of dried precipitate was obtained. Calculate the amount concentration of the lead(II) nitrate solution.

8. Compare the nature of science and the nature of technology, noting the key differences in the characteristics of these two forms of human endeavours.

Skills

9. What should you check before plugging in electrical equipment?
10. List some safety precautions for operating electrical equipment.
11. When studying chemical reactions, diagnostic tests are important to identify products (see Appendix C.4). Interpret the evidence in the photos below to identify the product or type of product formed in a chemical reaction.

halogen test

(a)

(b)

acidity test (using bromothymol blue)

(c)

(d)

ion colour test

(e)

(f)

12. List the general steps of a procedure to prepare a standard solution starting with a pure solid.
13. Titration is a common technological process used in different types of chemical analysis. List the main laboratory equipment needed to conduct a titration.

chapter

13 Redox Reactions

In this chapter

- Exploration: Cleaning Silver
- Case Study: Early Metallurgy
- Investigation 13.1: Single Replacement Reactions
- Web Activity: Henry Taube and Rudolph Marcus
- Web Activity: Redox Reaction
- Biology Connection: Metabolic Redox
- Investigation 13.2: Spontaneity of Redox Reactions
- Web Activity: Piercings: A Rash Decision
- Lab Exercise 13.A: Building a Redox Table
- Investigation 13.3: Predicting the Reaction of Sodium Metal (Demonstration)
- Lab Exercise 13.B: Oxidation States of Vanadium
- Web Activity: Catalytic Converters
- Case Study: Bleaching Wood Pulp
- Lab Exercise 13.C: Analyzing for Tin
- Web Activity: Imants Lauks
- Lab Exercise 13.D: Analyzing for Chromium in Steel
- Investigation 13.4: Analyzing a Hydrogen Peroxide Solution

Of all chemical changes, electrochemical (electron transfer) reactions are the most common in both living and nonliving systems. Photosynthesis, cellular respiration, and metabolism are all electrochemical processes. Technologies involving electrochemistry, such as combustion and the production of metals from their ores, have been used for thousands of years. In the development of these applications, the technology was successfully developed long before there was any scientific understanding of the processes. In other words, technology led science. More recently, however, a sophisticated understanding of modern electrochemistry has led to the invention of modern technologies such as aureate (gold-like) plating of coins (**Figure 1**), and the development of fuel cells and biosensors. Today, science and technology nurture each other in a symbiotic relationship.

Knowledge of electrochemistry will help you connect and clarify many seemingly unrelated reactions, and understand the interactions of science and technology. For example, paper for this book is produced from trees that used photosynthesis reactions to grow. Harvesting trees requires machinery made from steel, which is produced by the electrochemical reduction of iron ore. The energy used to run the machines in a pulp mill comes from the combustion of fossil fuels. Electrochemical reactions play a role in the production of paper from wood pulp. Photographs used in books may involve the reduction of silver ions to silver metal to form a negative image, which is printed using metal plates made by electrochemical reactions. All of the people involved, from those who harvest the trees to those who read the book, metabolize food to live and work. An understanding of electrochemistry will give you a broader comprehension of many chemical reactions and their importance in both living and nonliving systems.

STARTING Points

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

1. What are the key theoretical concepts that distinguish electrochemical reactions from other kinds of chemical reactions?
2. How can you predict whether or not a mixture of chemicals will react?
3. What are the similarities and differences between redox stoichiometry and other stoichiometry that you have learned?

Career Connections:
Materials/Metallurgical Engineer; Conservator

Figure 1
The aureate plating on the $1 and $2 coins gives them their golden colour. This plating process was invented in Fort Saskatchewan, Alberta, at the Sherritt Gordon plant.

Exploration Cleaning Silver

Have you ever noticed how silver becomes darkened and cloudy over time? This dark tarnish is mainly silver sulfide. The sulfur may come from several sources: air, which contains small amounts of hydrogen sulfide from industrial operations or from the decomposition of organic matter; natural gas, which contains a sulfur compound to give the odourless methane a noticeable odour; and some food items, including egg whites, mustard, and mayonnaise.

There are several technological solutions to restore the silvery appearance of tarnished silverware. Many silver-cleaning mixtures contain abrasives that are used to scour off the tarnish. However, these cleaners can remove the silver as well. A better technological process is to convert the silver sulfide back to silver metal. A common household remedy based on this approach is to react the tarnish with aluminium in a hot solution of baking soda and table salt.

Materials: tarnished silverware such as a small spoon, 400 or 600 mL beaker, piece of aluminium foil about 5 cm by 5 cm, hot plate, stirring rod, measuring spoon, tongs, baking soda, table salt, tap water

Do not touch the surface of the hot plate. Switch off the hot plate immediately after use.

- Fill the beaker about three-quarters full with tap water.
- Add about one teaspoon each of baking soda and table salt to the water. Stir to dissolve.
- Heat the solution on the hot plate to near boiling and then turn off the hot plate.

(a) Describe the appearance of the tarnished silver object and the aluminium foil.

- Use the tarnished silver object to push the aluminium foil to the bottom of the beaker. Make sure the silver object remains in contact with the foil.
- Observe any changes immediately and after several minutes.
- Use the tongs to remove the silver object and the aluminium foil.

(b) Describe the final appearance of the silver object and the aluminium foil.

(c) Write a balanced chemical equation for the single replacement reaction of solid silver sulfide and aluminium. How well does this equation explain your observations?

(d) Evaluate this technological process for cleaning tarnished silver.

- When cool, dispose of the solution down the sink and put the aluminium foil into the regular garbage.

13.1 Oxidation and Reduction

In prehistoric times, people learned to extract metals from rocks and minerals (**Figure 1**). This discovery initiated both the technology of metallurgy and humanity's progression from the Stone Age, through the Bronze Age and the Iron Age, to our increasingly technological modern age. Only a few metals, such as gold and silver, exist naturally in the form of a pure element. Most metals exist in a variety of compounds mixed with other substances in rocks called ores. *Metallurgy* is the science and technology of extracting metals from their naturally occurring compounds and adapting these metals for useful purposes. For some metals, the basic procedures are quite simple and were developed early in human history; for others, more complex procedures have been developed more recently. Making steel requires higher temperatures than those provided by a simple wood fire; therefore, this technology developed much later than the making of copper and bronze. A relatively recent example is the production of aluminium. This requires the technology to produce current electricity, which was not discovered until the 1800s. In all of these examples, from copper to aluminium, the technology was developed to solve practical problems before there was any scientific understanding of the processes involved.

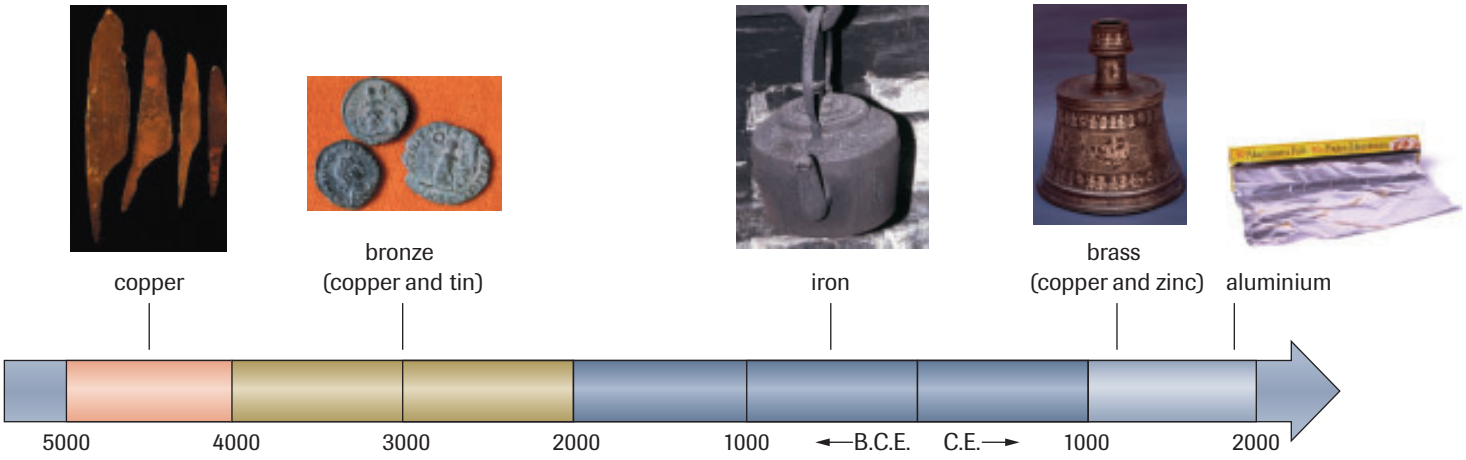

Figure 1
The technology of metallurgy has a long history, preceding by thousands of years the scientific understanding of the processes.

CAREER CONNECTION

Materials/Metallurgical Engineer

Being a Materials/Metallurgical Engineer is a challenging and rewarding career. The job involves learning the properties of materials, as well as developing new materials to meet specific requirements. Materials/Metallurgical Engineers also study and develop solutions for material fractures and breakages.

Read about the experiences of Nalaine Morin of the Tahltan First Nation, a metallurgical engineer.

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From metallurgy, the term *reduction* came to be associated with producing metals from their compounds. For example, iron(III) oxide is "reduced" by carbon monoxide gas to iron metal. Tin and copper metals are other examples where a metal compound is reduced to the metal.

$$Fe_2O_3(s) + 3\,CO(g) \rightarrow 2\,Fe(s) + 3\,CO_2(g)$$
$$SnO_2(s) + C(s) \rightarrow Sn(s) + CO_2(g)$$
$$CuS(s) + H_2(g) \rightarrow Cu(s) + H_2S(g)$$

As you can see from these chemical equations, a substance called a *reducing agent* causes or promotes the reduction of a metal compound to an elemental metal. In the preceding examples, carbon monoxide is the reducing agent for the production of iron from iron(III) oxide, carbon (charcoal) is the reducing agent for the production of tin from tin(IV) oxide, and hydrogen is the reducing agent for the production of copper from copper(II) sulfide. These are three of the most common reducing agents used in metallurgical processes.

Although the discovery of fire occurred much earlier than that of metal refining, both discoveries advanced the development of civilization significantly. There are also important similarities in the chemistry behind these technological developments. Of course, it does not require a detailed scientific understanding of the processes to use fire to refine metals (**Figure 2**). Only in the 18th century did we realize the role of oxygen in burning. Understanding the connection between corrosion and burning is an even more recent development. Scientists now understand that corrosion, including the rusting of metals, is similar to combustion, although corrosion reactions occur more slowly. Historically, *corrosion* was considered to be the spontaneous reaction of metals with air (oxygen) to form metal compounds (such as rust). In effect, corrosion was returning the metal to its natural state as a compound and, therefore, can be considered to be the opposite of metallurgy. Chemists eventually called the reactions of substances with oxygen, whether they were the explosive combustion of gunpowder, the burning of wood, or the slow corrosion of iron, *oxidation*. As the study of chemistry developed, chemists realized that oxygen was not the only substance that could cause reactions similar to oxidation reactions. For example, metals can be converted to compounds by most nonmetals and by some other substances as well. The rapid reaction process we call burning may even take place with gases other than oxygen, such as chlorine or bromine (**Figure 3**). The term "oxidation" has been extended beyond reactions with oxygen to include a wide range of combustion and corrosion reactions, such as the following:

$$2\,Mg(s) + O_2(g) \rightarrow 2\,MgO(s)$$
$$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)$$
$$Cu(s) + Br_2(g) \rightarrow CuBr_2(s)$$

A substance that causes or promotes the oxidation of a metal to produce a metal compound is called an *oxidizing agent*. In the reactions shown above, the oxidizing agents are oxygen, chlorine, and bromine. As you will see, an understanding of reduction and oxidation is necessary to explain many seemingly unrelated chemical reactions.

Figure 2
Making samurai swords requires a special type of fire (hardwood coals and bellows) to produce the higher temperatures required. This was a technological development long before any scientific understanding.

Figure 3
Copper metal is oxidized by reactive nonmetals such as bromine.

Practice

1. Using the historical context of metallurgy and corrosion, write an empirical definition for each of the following terms:
   (a) reduction
   (b) oxidation
   (c) oxidizing agent
   (d) reducing agent
   (e) metallurgy
   (f) corrosion
2. For each of the following, classify the reaction of the metal or metal compound in the historical context of reduction or oxidation, and identify the oxidizing agent or the reducing agent.
   (a) $4\,Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$
   (b) $2\,PbO(s) + C(s) \rightarrow 2\,Pb(s) + CO_2(g)$
   (c) $NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(l)$
   (d) $Sn(s) + Br_2(l) \rightarrow SnBr_2(s)$
   (e) $Fe_2O_3(s) + 3\,CO(g) \rightarrow 2\,Fe(s) + 3\,CO_2(g)$
   (f) $Cu(s) + 4\,HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,H_2O(l) + 2\,NO_2(g)$
3. List three reducing agents used in metallurgy.
4. What class of elements behaves as oxidizing agents for metals?
5. In the history of metallurgy, which came first, technological applications or scientific understanding? Elaborate on your answer.
6. Technologies that are intended to provide useful products and processes usually have unintended consequences. Using previous knowledge, list some unintended consequences that result from the production and refining of metals.

DID YOU KNOW?

Putting Out Class D Fires

A Class D fire includes combustible metals such as magnesium and the alkali metals. These metals burn at very high temperatures and water can make the fire much worse because of violent reactions. Carbon dioxide extinguishers don't help either since magnesium burns very well in carbon dioxide. So how can you put out such a fire? Sand is a simple option, but a special fire extinguisher such as MET-L-X, which contains sodium chloride, is the preferred method.

Case Study

Early Metallurgy

Metallurgy, which is the process of extracting metals from ores and forming them into useful objects, is an example of an early technology that was developed to solve practical problems. There is considerable archeological evidence that early humans discovered that gold, silver, and copper occurred in their natural state as nuggets or veins in rocks thousands of years ago. Stone tools were used to extract these metals from rocks and to hammer them into various objects. In particular, North American Aboriginal peoples developed the technology to extract copper from large copper pits in the Lake Superior region. The copper was used to make various ornaments, tools, and weapons. The problem was that the use of naturally occurring metals was limited to areas in which these metals were easily unearthed.

Over six thousand years ago, a new technology emerged when humans discovered that an extremely hot fire built on certain greenish rocks produced nuggets of solid copper in the cooling ashes. The extraction of metals from ores by heating is called *smelting*. Smelting copper ore to separate the copper from copper-bearing ore minerals, such as green malachite, meant that copper became much more widely used. There is evidence that smelting was discovered around 4500 B.C.E. in the Middle East because copper ornaments became more common after that time.

Since the ores of different metals often occur together, humans discovered that the metal smelted from a mixture of ores was much harder than pure copper. Smelting a mixture of copper and tin ores formed a hard copper–tin alloy known as *bronze*. Blades made from bronze could hold an edge very well and, if necessary, could be pounded back into shape. Bronze was one of the first metallic alloys widely used for containers, tools, weapons (**Figure 4**), and armour. The technology of smelting copper and formulating bronze diffused across Europe during the period of history known as the Bronze Age.

Figure 4
Bronze spearheads from the third millennium B.C.E.

The Bronze Age continued until humans developed the technology for smelting iron, which ushered in the Iron Age.

Case Study Questions

1. Is the discovery of metallurgy a scientific or technological achievement? Justify your answer.
2. What kinds of practical problems were solved or improved with the use of metals versus stone or wood? What new problems were created with the development of metal implements?
3. The following reaction equation represents the ancient process for smelting copper from malachite, $Cu_2CO_3(OH)_2(s)$, in a wood fire. Identify the reducing agent and the substance reduced.

$$Cu_2CO_3(OH)_2(s) + 2\,CO(g) \rightarrow 2\,Cu(s) + H_2O(g) + 3\,CO_2(g)$$

Extension

4. How was the process of trial and error used by early peoples to extract metals from their ores?

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INVESTIGATION 13.1 *Introduction*

Single Replacement Reactions

This investigation is a review of single replacement reactions in preparation for the development of a theory of oxidation and reduction. As part of the Design, include diagnostic tests (as in Appendix C.4) for the predicted products.

Purpose

The purpose of this investigation is to use the single replacement reaction generalization to predict and analyze the reactants and products.

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	○ Materials	● Evaluation (1)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Problem

What are the products of the single replacement reactions for the following pairs of reactants?

(a) copper and aqueous silver nitrate
(b) aqueous chlorine and aqueous sodium bromide
(c) magnesium and hydrochloric acid
(d) zinc and aqueous copper(II) sulfate
(e) aqueous chlorine and aqueous potassium iodide

To perform this investigation, turn to page 601.

WEB Activity

Canadian Achievers—Henry Taube and Rudolph Marcus

Henry Taube (**Figure 5(a)**) was born and educated in Saskatchewan. Rudolph Marcus (**Figure 5(b)**) was born and educated in Quebec. Taube and Marcus both contributed to the theory of electron transfer reactions. Each received a Nobel Prize in Chemistry, in 1983 and 1992, respectively, for their work.

1. In one sentence, describe the work done by each chemist as cited by the Nobel Committee.
2. Describe one difference between Taube's and Marcus' work.

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Figure 5
(a) Henry Taube (1915–2005)
(b) Rudolph Marcus (1923–)

Electron Transfer Theory

Single replacement reactions are reactions in which one element replaces another element in a compound. These reactions are useful to investigate first because they provide a relatively simple introduction to the modern theoretical definitions of oxidation and reduction. Imagine that a reaction is a combination of two parts called *half-reactions*. A half-reaction represents what is happening to one reactant in an overall reaction. It tells only part of the story. Another half-reaction is required to complete the description of the reaction. Splitting a chemical reaction equation into two parts not only makes the explanations simpler, but also leads to some important applications, which are discussed later in this unit.

For example, when zinc metal is placed into a hydrochloric acid solution, gas bubbles form as the zinc slowly dissolves (**Figure 6**). Diagnostic tests show that the gas is hydrogen and that zinc ions are present in the resulting solution. Notice that zinc metal is oxidized to zinc chloride. This is a corrosion of zinc caused by the hydrochloric acid.

$$Zn(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

What happens to the zinc and what happens to the hydrochloric acid? We can look at half-reactions to answer these questions. The zinc atoms in the solid, Zn(s), are converted to zinc ions in solution, $Zn^{2+}(aq)$. Atomic theory requires that the zinc atoms lose two electrons, as shown by the following half-reaction equation:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$$

Simultaneously, hydrogen ions in the solution gain electrons and are converted into hydrogen gas, as shown below:

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$$

Notice that both of these half-reaction equations, or half-reactions, are balanced by mass (same number of atoms/ions of each element on both sides) and by charge (same total charge on both sides). A **half-reaction** is a balanced chemical equation that represents either a loss or gain of electrons by a substance.

In a laboratory, single replacement reactions in aqueous solution are easier to study than the metallurgy or corrosion reactions discussed earlier in this chapter. However, all of these reactions share a common feature: ions are converted to atoms and atoms are converted to ions. For example, consider the reduction of aqueous silver nitrate to silver metal in the presence of solid copper (**Figure 7** on page 562). According to atomic theory, silver atoms are electrically neutral particles ($47p^+$, $47e^-$) and silver ions are

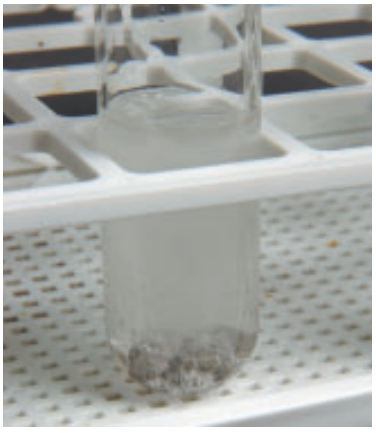
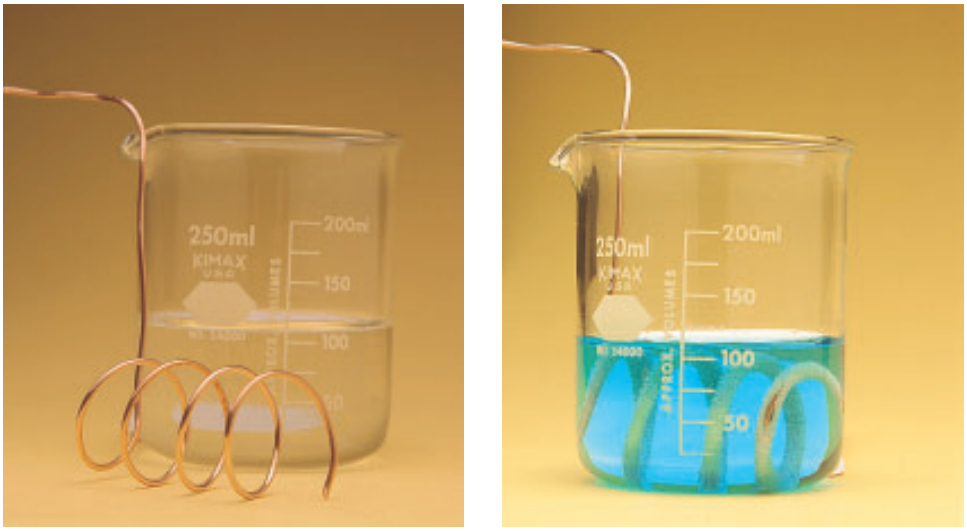


Figure 6
A common single replacement reaction is the reaction of active metals with an acid, such as zinc with hydrochloric acid.

Figure 7

A piece of copper before it is placed into a beaker of silver nitrate solution (left). Note the changes after the reaction has occurred (right). The blue colour of the solution indicates $Cu^{2+}(aq)$ ions are present.



Learning Tip

A common difficulty in writing half-reaction equations is deciding on which side of the equation the electrons should appear. There are two ways to approach this. You can use your theoretical knowledge of atoms and ions to determine whether the species is losing or gaining electrons. The alternative is to add up the electric charges on both sides of the equation arrow. The total must be the same on both sides. Try this for the half-reaction equations on this page.

charged particles ($47p^+, 46e^-$). Therefore, in this reaction, a single electron is required to convert a silver ion into a silver atom. The following half-reaction equation explains the reduction of silver ions using the theoretical rules for atoms and ions:

$$Ag^+(aq) + e^- \rightarrow Ag^0(s) \qquad \text{(reduction)}$$

According to modern theory, the gain of electrons is called ***reduction****.*

Although this theoretical definition of reduction agrees with current atomic theory, it does not explain where the electrons come from. As crystals of silver metal are produced, the solution becomes blue, indicating that copper atoms are being converted to copper(II) ions. According to atomic theory, copper atoms ($29p^+, 29e^-$) must each be losing two electrons as they form copper(II) ions ($29p^+, 27e^-$):

$$Cu^0(s) \rightarrow Cu^{2+}(aq) + 2\,e^- \qquad \text{(oxidation)}$$

According to modern theory, the loss of electrons is called ***oxidation****.*

Evidence shows that the silver-coloured solid and the blue colour of the solution are simultaneously formed near the surface of the copper metal. Scientists believe, therefore, that the electrons required by the silver ions are supplied when silver ions collide with copper atoms on the metal surface.

The theory of electron transfer requires that the *total number of electrons gained in a reaction must equal the total number of electrons lost*, and that oxidation and reduction are separate processes. This theoretical description requires oxidation and reduction to occur simultaneously rather than sequentially. Oxidation–reduction reactions are often simply called "redox" reactions. A **redox** (**red**uction–**ox**idation) **reaction** is a chemical reaction in which electrons are transferred between entities.

The equations for reduction and oxidation half-reactions, and the overall (net) ionic equation summarize the electron transfer that is believed to take place during a redox reaction. As in other chemical reactions, the net equation must be balanced. We will learn how to write balanced half-reactions and net equations in Sample Problem 13.1.

DID YOU KNOW?

Redox Mnemonics

A mnemonic is a word or group of words used to help remember information. "LEO the lion says GER" is a mnemonic to help remember that "Loss of Electrons is Oxidation" and "Gain of Electrons is Reduction." Another mnemonic is "OIL RIG," which translates as "Oxidation Is Loss, Reduction Is Gain."

WEB Activity

Simulation—Redox Reaction

Use the computer simulation of the reaction between lead atoms and silver ions to determine which entity loses electrons and which gains electrons. Note the number of electrons lost or gained by each kind of atom/ion. Write the oxidation and reduction half-reaction equations.

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SAMPLE problem 13.1

Write the balanced half-reaction equations and a balanced net equation for the reaction of copper metal with aqueous silver nitrate.

To show that the number of electrons gained equals the number of electrons lost in two half-reaction equations, it may be necessary to multiply one or both half-reaction equations by a coefficient to balance the electrons. In this example, the silver half-reaction equation must be multiplied by 2.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^- \quad \text{(two electrons lost by one atom)}$$

$$2\,[Ag^+(aq) + e^- \rightarrow Ag(s)] \quad \text{(two electrons gained by two ions)}$$

Now, add the half-reaction equations and cancel the terms that appear on both sides of the equation to obtain the net ionic equation.

$$2\,Ag^+(aq) + \cancel{2e^-} + Cu(s) \rightarrow 2\,Ag(s) + Cu^{2+}(aq) + \cancel{2e^-}$$

$$2\,Ag^+(aq) + Cu(s) \rightarrow 2\,Ag(s) + Cu^{2+}(aq)$$

Silver ions are reduced to silver metal by reaction with copper metal. Simultaneously, copper metal is oxidized to copper(II) ions by reaction with silver ions (**Figure 8**).

oxidized to metal ion

$$2\,Ag^+(aq) + Cu(s) \rightarrow 2\,Ag(s) + Cu^{2+}(aq)$$

reduced to metal

COMMUNICATION example 1

Write and label two balanced half-reaction equations to describe the reaction of zinc metal with aqueous lead(II) nitrate, as given by the following chemical equation:

$$Zn(s) + Pb(NO_3)_2(aq) \rightarrow Pb(s) + Zn(NO_3)_2(aq)$$

Solution

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^- \quad \text{(oxidation)}$$

$$Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s) \quad \text{(reduction)}$$

To evaluate the theory of oxidation and reduction, you should look at its logical consistency with other accepted theories and definitions. The theoretical definitions of oxidation and reduction are consistent with the historical, empirical definitions presented earlier in this chapter; for example, a compound is reduced to a metal and a metal is oxidized to form a compound. Redox theory is also consistent with accepted atomic theory and the collision–reaction theory. Most importantly, redox theory explains the observations made by scientists.

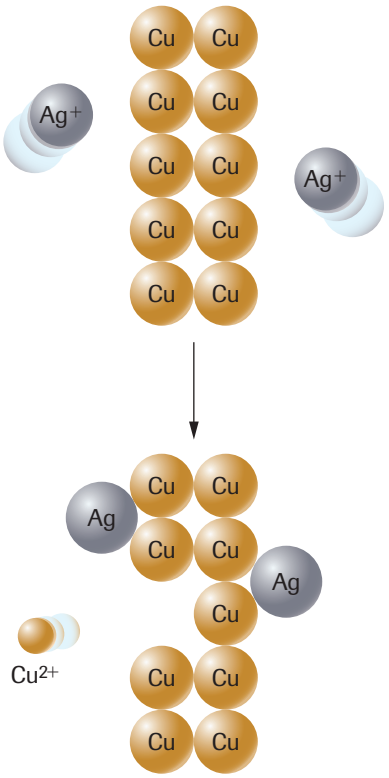

Figure 8
A model of the reaction of copper metal and silver nitrate solution illustrates aqueous silver ions reacting at the surface of a copper strip.

Learning Tip

When you are cancelling terms for a net ionic equation, the terms must be identical, including their states of matter. Electrons must always cancel completely. This is because the electrons that appear in each half-reaction equation are the same electrons. They are the electrons that transfer from one entity to another.

DID YOU KNOW ?

Compartmentalization

The tradition in Western science is generally to break large systems down into smaller and smaller pieces to describe and explain them. Science is broken down into various areas such as biology, chemistry, and physics, which can then be further subdivided. One compartment of chemistry is redox, which includes several subcategories.

In contrast, Aboriginal science is more holistic: the whole of nature, from the smallest parts to the cosmos, is connected. Viewing nature this way gives us a different perspective on current problems such as pollution and climate change. Recently, there is a trend in Western science toward a more holistic view after decades of compartmentalization.

Figure 9
The reduction of iron(III) oxide by aluminium is called the "thermite" reaction. Because this reaction is rapid and very exothermic, molten white-hot iron is produced. Here a falling aluminium wrench momentarily sparks a thermite reaction when it strikes a rusted iron block.

SUMMARY Electron Transfer Theory

- A *redox reaction* is a chemical reaction in which electrons are transferred between entities.
- The total number of electrons gained in the reduction equals the total number of electrons lost in the oxidation.
- *Reduction* is a process in which electrons are gained by an entity.
- *Oxidation* is a process in which electrons are lost by an entity.
- Both reduction and oxidation are represented by balanced half-reaction equations.

Practice

7. Write a theoretical definition for each of the following terms:
(a) redox reaction (b) reduction (c) oxidation

8. Write a pair of balanced half-reaction equations—one showing a gain of electrons and one showing a loss of electrons—for each of the following reactions:
(a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(b) $Mg(s) + 2\,H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

9. For each of the following, write and label the oxidation and reduction half-reaction equations. Ignore spectator ions.
(a) $Ni(s) + Cu(NO_3)_2(aq) \rightarrow Cu(s) + Ni(NO_3)_2(aq)$
(b) $Pb(s) + Cu(NO_3)_2(aq) \rightarrow Cu(s) + Pb(NO_3)_2(aq)$
(c) $Ca(s) + 2\,HNO_3(aq) \rightarrow H_2(g) + Ca(NO_3)_2(aq)$
(d) $2\,Al(s) + Fe_2O_3(s) \rightarrow 2\,Fe(l) + Al_2O_3(s)$ (**Figure 9**)

10. We have only looked at one type of single replacement reaction—a metal displacing another metal from an ionic compound. A nonmetal can also displace another nonmetal from an ionic compound. For example,

$Cl_2(aq) + 2\,NaI(aq) \rightarrow I_2(s) + 2\,NaCl(aq)$

Using your knowledge of atoms and ions and the ideas presented in this chapter, write a pair of balanced half-reaction equations for this reaction—one showing a gain of electrons and one showing a loss of electrons.

11. Ionic compounds can react in double replacement reactions. For example,

$FeCl_3(aq) + 3\,NaOH(aq) \rightarrow Fe(OH)_3(s) + 3\,NaCl(aq)$

According to ideas discussed in this chapter, has a redox reaction taken place in the reaction above? Explain your answer.

Writing Complex Half-Reaction Equations

Although most metals and nonmetals have relatively simple half-reaction equations, polyatomic ions and molecular compounds undergo more complicated oxidation and reduction processes. In most of these processes, the reaction takes place in an aqueous solution that is very often acidic or basic. Experimental evidence shows that water molecules, hydrogen ions, and hydroxide ions play an important role in these half-reactions. A method of writing half-reactions for polyatomic ions and molecular compounds requires that water molecules and hydrogen or hydroxide ions be included. This method, illustrated in the following sample problem, is sometimes called the "half-reaction" or "ion–electron" method.

SAMPLE problem 13.2

Nitrous acid can be reduced in an acidic solution to form nitrogen monoxide gas. What is the reduction half-reaction for nitrous acid?

The first step is to write the reactants and products.

$$HNO_2(aq) \rightarrow NO(g)$$

If necessary, you should balance all atoms other than oxygen and hydrogen in this partial equation. In this example, there is only one nitrogen atom on each side.

Next, add water molecules, present in an aqueous solution, to balance the oxygen atoms.

$$HNO_2(aq) \rightarrow NO(g) + H_2O(l)$$

Because the reaction takes place in an acidic solution, hydrogen ions are available. These can be used to balance the hydrogen on both sides of the equation.

$$H^+(aq) + HNO_2(aq) \rightarrow NO(g) + H_2O(l)$$

At this stage, all of the atoms should be balanced, but the charge on both sides will not be balanced. Add an appropriate number of electrons to balance the charge. Because electrons carry a negative charge, they are always added to the less negative, or more positive, side of the half-reaction.

$$e^- + H^+(aq) + HNO_2(aq) \rightarrow NO(g) + H_2O(l)$$

This balanced half-reaction equation represents a gain of electrons, or a reduction of the nitrous acid. Check to make sure that both the atom symbols and the charge are balanced.

BIOLOGY CONNECTION

Metabolic Redox

There are many biological processes, including metabolism and cellular respiration, that are redox reactions. You will learn about them in a biology course.

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In a basic solution, the concentration of hydroxide ions greatly exceeds that of hydrogen ions. For basic solutions, we will develop the half-reaction as if it occurred in an acidic solution, and then convert the hydrogen ions into water molecules using hydroxide ions. This trick works because a hydrogen ion and a hydroxide ion react in a 1:1 ratio to form a water molecule. The following sample problem illustrates the procedure for writing half-reaction equations that occur in basic solutions.

Learning Tip

You can also balance half-reaction equations in a basic solution by following these steps.

1. Balance atoms other than oxygen and hydrogen.
2. Add hydroxide ions to balance the oxygen.
3. Add water to balance the hydrogen.
4. Add electrons to balance the charge.

The difficulty with this method is that adding hydroxide ions and water simultaneously affects both the oxygen and hydrogen count.

SAMPLE problem 13.3

Copper metal can be oxidized in a basic solution to form copper(I) oxide. What is the half-reaction for this process?

Following the same steps as before, we write the formula and balance the atoms, other than oxygen and hydrogen. Here, the copper atoms must be balanced.

$$2\,Cu(s) \rightarrow Cu_2O(s)$$

Next, balance the oxygen using water molecules and balance the hydrogen using hydrogen ions, assuming, for the moment, an acidic solution. Balance the charge using electrons.

$$H_2O(l) + 2\,Cu(s) \rightarrow Cu_2O(s) + 2\,H^+(aq) + 2\,e^-$$

Because the half-reaction occurs in a basic solution, add the same number of hydroxide ions as there are hydrogen ions to both sides of the equation. This is done to maintain the balance of mass and charge.

$$2\,OH^-(aq) + H_2O(l) + 2\,Cu(s) \rightarrow Cu_2O(s) + 2\,H^+(aq) + 2\,e^- + 2\,OH^-(aq)$$

Combine equal numbers of hydrogen ions and hydroxide ions to form water molecules.

$$2\,OH^-(aq) + H_2O(l) + 2\,Cu(s) \rightarrow Cu_2O(s) + 2\,H_2O(l) + 2\,e^-$$

Finally, cancel equal amounts of $H_2O(l)$ and anything else that is the same from both sides of the equation. Check that the atom symbols and charge are balanced.

$$2\,OH^-(aq) + \cancel{H_2O(l)} + 2\,Cu(s) \rightarrow Cu_2O(s) + \cancel{2}H_2O(l) + 2\,e^-$$
$$2\,OH^-(aq) + 2\,Cu(s) \rightarrow Cu_2O(s) + H_2O(l) + 2\,e^-$$

Learning Tip

Recall that loss of electrons is oxidation (LEO) and gain of electrons is reduction (GER).

COMMUNICATION example 2

Chlorine is converted to perchlorate ions in an acidic solution. Write the half-reaction equation. Is this half-reaction an oxidation or a reduction?

Solution

$$8\,H_2O(l) + Cl_2(aq) \rightarrow 2\,ClO_4^-(aq) + 16\,H^+(aq) + 14\,e^-$$

According to redox theory, this half-reaction is an oxidation.

COMMUNICATION example 3

Aqueous permanganate ions are reduced to solid manganese(IV) oxide in a basic solution. Write the half-reaction equation. Is the half-reaction an oxidation or a reduction?

Solution

$$4\,OH^-(aq) + 4\,H^+(aq) + MnO_4^-(aq) + 3\,e^- \rightarrow MnO_2(s) + 2\,H_2O(l) + 4\,OH^-(aq)$$
$$4\,H_2O(l) + MnO_4^-(aq) + 3\,e^- \rightarrow MnO_2(s) + 2\,H_2O(l) + 4\,OH^-(aq)$$
$$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \rightarrow MnO_2(s) + 4\,OH^-(aq)$$

According to redox theory, this half-reaction is a reduction.

EXTENSION

Redox Reactions

This short movie and the accompanying exercise will help you check your understanding of redox reactions.

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Practice

12. For each of the following, complete the half-reaction equation and classify it as an oxidation or a reduction.

(a) dinitrogen oxide to nitrogen gas in an acidic solution
(b) nitrite ions to nitrate ions in a basic solution
(c) silver(I) oxide to silver metal in a basic solution
(d) nitrate ions to nitrous acid in an acidic solution
(e) hydrogen gas to water in a basic solution

SUMMARY Writing Half-Reaction Equations

Step 1: Write the chemical formulas for the reactants and products.
Step 2: Balance all atoms, other than O and H.
Step 3: Balance O by adding $H_2O(l)$.
Step 4: Balance H by adding $H^+(aq)$.
Step 5: Balance the charge on each side by adding e^- and cancel anything that is the same on both sides.

For basic solutions only:
Step 6: Add $OH^-(aq)$ to both sides to equal the number of $H^+(aq)$ present.
Step 7: Combine $H^+(aq)$ and $OH^-(aq)$ on the same side to form $H_2O(l)$. Cancel equal amounts of $H_2O(l)$ from both sides.

Section 13.1 Questions

1. Compare the historical empirical definitions of oxidation and reduction with the modern theoretical definitions.
2. According to modern theory, explain what is meant by a redox reaction.
3. What is a half-reaction and how does it relate to the overall chemical reaction equation?
4. Describe what happens to the electrons that are lost by one entity in a redox reaction.
5. What common type of chemical reaction is generally not a redox reaction? Include a brief theoretical explanation.
6. Write and label a pair of balanced half-reaction equations for each of the following reactions.
   (a) $Pb(s) + Cu^{2+}(aq) \rightarrow Pb^{2+}(aq) + Cu(s)$
   (b) $Cl_2(aq) + 2\,Br^-(aq) \rightarrow 2\,Cl^-(aq) + Br_2(l)$
   (c) the removal of silver tarnish (**Figure 10**) in the single replacement reaction of silver sulfide solid with aluminium

Figure 10
If tarnished silver is placed on aluminium foil in a hot electrolyte solution, a redox reaction converts the tarnish back into silver metal.

7. For each of the following applications, complete the half-reaction equation and classify it as an oxidation or a reduction.
   (a) bacterial action in soil: ammonia to nitrite ions in an acidic environment
   (b) pulp and paper bleaching: hydrogen peroxide to water in an acidic solution
   (c) alkaline battery: manganese(IV) oxide to manganese(III) oxide in a basic environment

Extension

8. Photosynthesis is a complex electron-transfer process that is essential for almost all life forms on Earth. Write and label the half-reaction equations for the "light reaction" and the "dark reaction."

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9. One of the earliest technologies is the use of fire. There are various stories in many cultures about how people learned about fire, such as the North American Aboriginal story of how the coyote steals fire. These stories serve as metaphors for the technology that we use today. Summarize the legend of the coyote and fire. How does this metaphor relate to the goals and effects of technology today?

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10. Archaeometallurgy is the study of ancient metallurgy using modern analytical techniques (**Figure 11**). Give some examples of research in the field. What metals and time periods have been studied? Can a metal from one mine be distinguished from the same metal from another mine? How is this information used in archaeological studies?

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Figure 11
Aslihan Yener (left) pioneered the use of modern X-ray techniques to identify metals from as early as 8000 B.C.E.

13.2 Predicting Redox Reactions

Figure 1
Copper(II) ions react spontaneously with zinc metal. A copper(II) ion has a stronger attraction for the valence electrons of a zinc atom than zinc does.

Figure 2
When a strip of copper is placed in a solution of nickel(II) ions, the green nickel(II) ion colour remains and the copper metal does not react. Collisions between copper atoms and nickel(II) ions apparently do not result in the transfer of electrons.

A redox reaction may be explained as a transfer of valence electrons from one substance to another. Evidence indicates that the majority of atoms, molecules, and ions are stable and do not readily release electrons. Since two entities must be involved in an electron transfer, chemists explain this transfer as a competition for electrons. Using a tug-of-war analogy, each entity pulls on the same electrons. If one entity is able to pull electrons away from the other, a spontaneous reaction occurs (**Figure 1**). Otherwise, no reaction occurs (**Figure 2**). In the spontaneous reaction of copper(II) ions and zinc metal, the Cu^{2+} ion is electron deficient and pulls electrons from a Zn atom. We can explain the reaction evidence using the idea that Cu^{2+} "pulls harder" on Zn's electrons than Zn does. Cu^{2+} "wins" the two valence electrons from a Zn atom. A successful electron transfer has occurred.

Without mixing all possible reactants and observing any evidence of reaction, how can we predict if a reaction will occur? If a reaction occurs, what will be produced? The answers to these questions cannot be obtained easily using redox theory. By observing many successful and unsuccessful reactions, patterns emerge and empirical generalizations can be made.

Oxidizing and Reducing Agents

Before we look at these patterns, we need to define some terms commonly used by chemists. When discussing possible reactants and comparing their reactivities, it is customary and convenient to classify the reactants in a redox reaction. This classification originated historically, but is now defined theoretically in terms of an ability to lose or gain electrons. In any redox reaction, an electron transfer occurs. This means that one reactant is oxidized and one reactant is reduced.

e^-

	X	+	Y	→	products
electron change	loses (is oxidized)		gains (is reduced)		
Examples:	$Zn(s)$	+	$Cu^{2+}(aq)$	→	$Zn^{2+}(aq) + Cu(s)$
	$2\ Br^-(aq)$	+	$Cl_2(g)$	→	$Br_2(l) + 2\ Cl^-(aq)$

Rather than saying "the reactant that is oxidized" and "the reactant that is reduced," chemists use the terms reducing agent (RA) and oxidizing agent (OA). These terms originated in the early history of metallurgy and corrosion. For example, to "reduce" a larger volume of iron(III) oxide to a smaller volume of pure iron, a substance called a reducing agent was required, such as $CO(g)$.

reducing agent + $Fe_2O_3(s)$ → $Fe(s)$ + other products

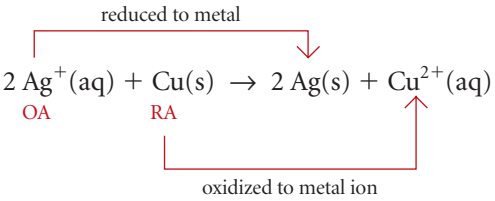
reduction

Similarly, oxidation was originally associated with an oxidizing agent. For example, a metal could be oxidized by certain substances called oxidizing agents. At first, oxygen was the only known oxidizing agent, but others (e.g., halogens) can also oxidize, or corrode, metals.

oxidation

oxidizing agent + $Mg(s)$ → $MgO(s)$ + other products

The terms oxidizing and reducing agents developed separately, long before any redox theory of electron transfer emerged. Today, chemists routinely think in terms of electron transfer to explain redox reactions. A redox reaction is recognized as an electron transfer between an oxidizing agent and a reducing agent (**Figure 3**). Based on this idea, chemists say that a **reducing agent** causes reduction by donating (losing) electrons to another substance in a redox reaction. During this process, the reducing agent is oxidized. An **oxidizing agent** causes oxidation by removing (gaining) electrons from another substance in a redox reaction. During this process, the oxidizing agent is reduced. *It is important to note that oxidation and reduction are processes, and oxidizing agents and reducing agents are substances.* For example,



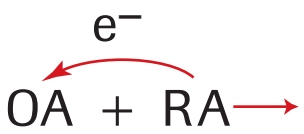


Figure 3
In all redox reactions, electrons are transferred from a reducing agent (RA) to an oxidizing agent (OA).

INVESTIGATION 13.2 *Introduction*

Spontaneity of Redox Reactions

In previous units in this textbook, we assumed that all chemical reactions are spontaneous; that is, they occur once the reactants are placed in contact, without a continuous addition of energy to the system. Spontaneous redox reactions in solution generally provide visible evidence of a reaction within a few minutes.

Purpose

The purpose of this investigation is to test the assumption that all single replacement reactions are spontaneous.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (1, 2, 3)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

Problem

Which combinations of copper, lead, silver, and zinc metals and their aqueous metal ion solutions produce spontaneous reactions?

Design

A drop of each solution is placed in separate locations on a clean area of each of the four metal strips.

To perform this investigation, turn to page 602.

Development of a Redox Table

Some redox reactions, such as single replacement reactions, are easy to study experimentally. The evidence of a reaction is immediately obvious and the interpretation of an electron transfer is relatively simple. In the past, you have generally assumed that all single replacement reactions are spontaneous. However, the evidence you obtained in Investigation 13.2 clearly shows that this assumption is unacceptable as only six of the combinations led to a reaction. The question that arises is, "How do you know when a chemical reaction will occur spontaneously without actually doing the reaction?"

Let's look at the combinations of metals and metal ions used in Investigation 13.2. Copper, lead, silver, and zinc metals were combined one at a time with each of copper(II), lead(II), silver, and zinc ion solutions. Based on the evidence collected, we can rank the ability of the metal ions to react with the metals (**Table 1**).

Table 1 Reactivities of Metal Ions with Metals

Ions	$Ag^+(aq)$	$Cu^{2+}(aq)$	$Pb^{2+}(aq)$	$Zn^{2+}(aq)$
reacted with	Cu(s), Pb(s), Zn(s)	Pb(s), Zn(s)	Zn(s)	none
number of reactions	3	2	1	0
reactivity order	most →			least

Learning Tip

If a positively charged metal ion reacts, then it is usually converted to a metal atom. According to redox theory, this requires a gain of electrons and hence the metal ion is behaving as an oxidizing agent. Similarly, if a metal atom reacts, then it is always converted to a positively charged ion by losing electrons. Metals always behave as reducing agents.

The most reactive metal ion, $Ag^+(aq)$, has the greatest tendency to gain electrons. On the other hand, $Zn^{2+}(aq)$ shows no tendency to gain electrons in the combinations tested. Therefore, the order of reactivity is also the order of strength as oxidizing agents.

strongest oxidizing agent $Ag^+(aq) + e^- \rightarrow Ag(s)$

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$

$Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)$

weakest oxidizing agent $Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$

The order of reactivity of the four metals can be obtained in a similar way (**Table 2**).

Table 2 Reactivities of Metals with Metal Ions

Metals	Zn(s)	Pb(s)	Cu(s)	Ag(s)
reacted with	$Ag^+(aq)$, $Cu^{2+}(aq)$, $Pb^{2+}(aq)$	$Ag^+(aq)$, $Cu^{2+}(aq)$	$Ag^+(aq)$	none
number of reactions	3	2	1	0
reactivity order	most →			least

The most reactive metal, Zn(s), has the greatest tendency to lose electrons and Ag(s) shows no tendency to lose electrons in the combinations tested. Metals behave as reducing agents and so Zn(s) is the strongest reducing agent among those tested.

strongest reducing agent $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$

$Pb(s) \rightarrow Pb^{2+}(aq) + 2\,e^-$

$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$

weakest reducing agent $Ag(s) \rightarrow Ag^+(aq) + e^-$

In these four reactions, the metal ions are the oxidizing agents and the silver ion is the strongest oxidizing agent (SOA) because it is the most reactive in our group. The two lists can be summarized using a single set of half-reactions (**Table 3**).

Table 3 Relative Strengths of Oxidizing and Reducing Agents

		OA $+ n\,e^- \rightleftarrows$ RA		
decreasing reactivity of oxidizing agents	SOA ↓	$Ag^+(aq) + e^- \rightleftarrows Ag(s)$ $Cu^{2+}(aq) + 2\,e^- \rightleftarrows Cu(s)$ $Pb^{2+}(aq) + 2\,e^- \rightleftarrows Pb(s)$ $Zn^{2+}(aq) + 2\,e^- \rightleftarrows Zn(s)$	↑ SRA	decreasing reactivity of reducing agents

Learning Tip

The double arrows indicate that half-reactions may be read from left to right (top arrow) or from right to left (bottom arrow).

In **Table 3**, the metal ions are on the left side of the equations and the metal atoms are on the right side. For metal ions (the oxidizing agents), the half-reaction equations are read from left to right in the table. For metal atoms (the reducing agents), the half-reaction equations are read from right to left.

WEB Activity

Web Quest—Piercings: A Rash Decision

Most Canadians wear some type of jewellery. However, some individuals react to their jewellery. This Web Quest explores the chemistry behind these reactions. What can you do to protect yourself from your jewellery?

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SUMMARY Oxidizing and Reducing Agents

- An *oxidizing agent* causes oxidation by removing (gaining) electrons from another substance in a redox reaction. In this process, the oxidizing agent is reduced.
- A *reducing agent* promotes reduction by donating (losing) electrons to another substance in a redox reaction. In this process, the reducing agent is oxidized.
- A table of relative strengths of oxidizing and reducing agents—more simply known as a redox table—is, by convention, listed as reductions (from left to right) in the form: **OA** + $n\,e^- \rightleftarrows$ **RA**, with the strongest oxidizing agent at the top left and strongest reducing agent at the bottom right of the table.

Learning Tip

If a nonmetal reacts, then it is usually converted to a negatively charged ion by gaining electrons. Nonmetals always behave as oxidizing agents. Negatively charged nonmetal ions lose electrons when they react; therefore, nonmetal ions behave as reducing agents.

Practice

1. Oxidation and reduction are processes, and oxidizing agents and reducing agents are substances. Explain this statement.
2. If a substance is a very strong oxidizing agent, what does this mean in terms of electrons?
3. If a substance is a very strong reducing agent, what does this mean in terms of electrons?
4. The terms, oxidizing agent and reducing agent, may be confusing especially when used in conjunction with the terms, oxidation and reduction. The key to avoiding confusion is to focus on the word "agent." Use a dictionary or write a definition in your own words of the term "agent." How can a banker (loans agent) be used as an analogy for a reducing agent?

Refer to **Table 1** (on page 569), and **Tables 2** and **3** (on page 570) to answer questions 5 to 9.

5. List the metal(s) that react spontaneously with a copper(II) ion solution.
6. Which metal(s) did not appear to react with a copper(II) ion solution?
7. Start with the position of $Cu^{2+}(aq)$ in **Table 3** and note the position of the metal(s) that reacted and the metal(s) that did not react. For a metal that reacts spontaneously with $Cu^{2+}(aq)$, where does the metal appear on a table of reduction half-reactions (**Table 3**)?
8. Repeat questions 5 to 7 for the $Pb^{2+}(aq)$ ion.
9. Your answers to questions 7 and 8 form an empirical hypothesis that can be tested by making predictions for the other metal ions. Use **Table 3** to predict which of the reactions should be spontaneous. According to the evidence from Investigation 13.2, are your predictions correct? Is your hypothesis verified?

10. An experiment similar to the example of metals and metal ions was conducted using halogens and halide ions. Prepare a redox table of half-reaction equations similar to **Table 3** for the halogens.

Evidence

Only three combinations produced evidence of a reaction (**Figure 4**, **Table 4**).

Table 4 Reactions of Halogens with Solutions of Halides

	$Br_2(aq)$	$Cl_2(aq)$	$I_2(aq)$
$Br^-(aq)$	no reaction	yellow-brown	no reaction
$Cl^-(aq)$	no reaction	no reaction	no reaction
$I^-(aq)$	pink/purple	pink/purple	no reaction

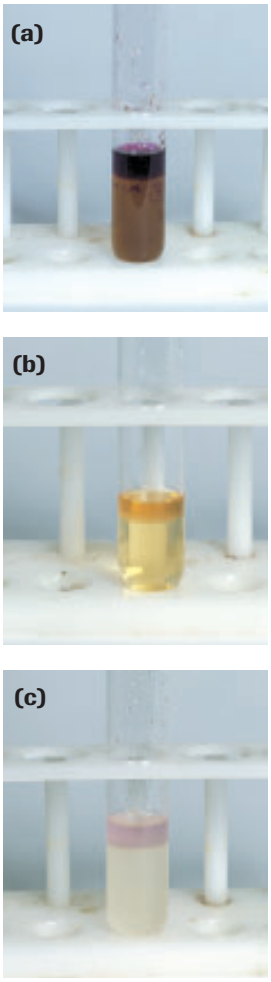

Figure 4
None of the combinations of aqueous solutions of chlorine, bromine, and iodine with their corresponding halides show any evidence of reaction except for the reaction between **(a)** bromine and iodide ions, **(b)** chlorine and bromide ions, and **(c)** chlorine and iodide ions.

LAB EXERCISE 13.A

Building a Redox Table

Suppose that a research team is developing a table of relative strengths of oxidizing and reducing agents. One team member had completed an investigation summarized in **Table 3**, page 570, and another had completed the investigation reported in Practice question 10, page 571. A third member used the combination of metals, nonmetals, and solutions shown below. By completing this exercise, you will see how scientists have developed extensive tables of relative strengths of oxidizing and reducing agents.

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ○ Evidence
- ● Analysis
- ○ Evaluation

Purpose

The purpose of this lab exercise is to create an extended table of relative strengths of oxidizing and reducing agents.

Problem

What is the table of relative strengths of oxidizing and reducing agents for the combined results from three experiments?

Evidence

Table 5 Reactions of Metals and Nonmetals with Solutions of Ions

	$I_2(aq)$	$Cu^{2+}(aq)$	$Ag^+(aq)$	$Br_2(aq)$
$I^-(aq)$	X	X	✓	✓
Cu(s)	✓	X	✓	✓
Ag(s)	X	X	X	✓
$Br^-(aq)$	X	X	X	X

X no evidence of a redox reaction
✓ evidence redox reaction occurred

Analysis

(a) Use **Table 5** to construct a mini-redox table of just those substances.

(b) Compare **Table 3**, your analysis table from Practice question 10, and your table. Note that there are several substances that appear in two of these tables. Combine all three tables in one larger table showing the order of oxidizing and reducing agents.

DID YOU KNOW ?

Redox Table

The format of the redox table used in this textbook is very common. However, some books and references show a redox table as reversed (top to bottom), or list the oxidation and reduction half-reactions in alphabetical order or in order of strength of the agents.

The Spontaneity Rule

Evidence obtained from the study of many redox reactions has been used to establish a generalization, called the **redox spontaneity rule**. The redox spontaneity rule states that a spontaneous redox reaction occurs only if the oxidizing agent (OA) is above the reducing agent (RA) in a table of relative strengths of oxidizing and reducing agents. **Figure 5** illustrates how you can use the rule, along with a table of oxidizing and reducing agents, to predict whether a reaction is spontaneous or nonspontaneous (no reaction).

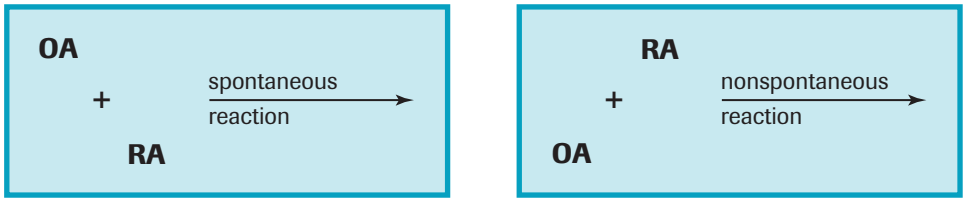

Figure 5
The redox spontaneity rule

Another Method for Building Redox Tables

Once a spontaneity rule is developed from experimental evidence, the rule may be used to generate redox tables. The evidence to be analyzed in this case is a net ionic equation, accompanied by observations of spontaneity. In the following method, the spontaneity rule, rather than the number of reactions observed, is used to order the oxidizing and reducing agents to produce a redox table. The procedure for this type of analysis and synthesis is illustrated by Sample Problem 13.4.

SAMPLE problem 13.4

Three reactions among indium, cobalt, palladium, and copper were investigated. The reaction equations below indicate that two spontaneous reactions occurred and only one combination did not react. Using these equations, construct a redox table of half-reaction equations showing the relative strengths of the oxidizing and reducing agents.

$3\ Co^{2+}(aq) + 2\ In(s) \rightarrow 2\ In^{3+}(aq) + 3\ Co(s)$ (spontaneous)

$Cu^{2+}(aq) + Co(s) \rightarrow Co^{2+}(aq) + Cu(s)$ (spontaneous)

$Cu^{2+}(aq) + Pd(s) \rightarrow$ no evidence of reaction (nonspontaneous)

To construct a redox table from this information, work with one equation at a time. Identify the oxidizing and reducing agents for the first reaction, and arrange them in two columns using the spontaneity rule. For the first reaction, this step is shown in **Figure 6(a)**. $Co^{2+}(aq)$ is the oxidizing agent and In(s) is the reducing agent. Since the reaction is spontaneous, the oxidizing agent is above the reducing agent in the list.

In the second reaction, $Cu^{2+}(aq)$ is the oxidizing agent and Co(s) is the reducing agent. This reaction is also spontaneous; therefore, $Cu^{2+}(aq)$ is above Co(s) in the list. Since a metal appears on the same line as its ion in a redox table, add Co(s) and extend the list as shown in **Figure 6(b)**.

No reaction occurs for the third pair of reactants. If a reaction had occurred, $Cu^{2+}(aq)$ would be the oxidizing agent and Pd(s) would be the reducing agent. As this reaction is not spontaneous, the oxidizing agent appears below the reducing agent. **Figure 6(c)** shows the list extended to include Pd(s). To complete the table, write balanced half-reaction equations for each oxidizing/reducing agent pair.

SOA

$Pd^{2+}(aq) + 2e^- \rightleftarrows Pd(s)$

$Cu^{2+}(aq) + 2e^- \rightleftarrows Cu(s)$

$Co^{2+}(aq) + 2e^- \rightleftarrows Co(s)$

$In^{3+}(aq) + 3e^- \rightleftarrows In(s)$ **SRA**

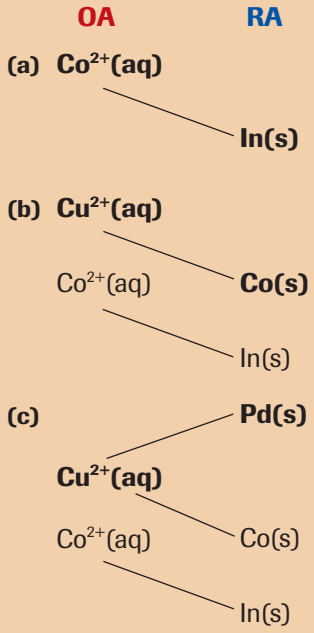

Figure 6
The relative position of a pair of oxidizing and reducing agents indicates whether a reaction will be spontaneous.

Practice

11. A student performed the following reactions. Construct a table of relative strengths of oxidizing and reducing agents.

$Co^{2+}(aq) + Zn(s) \rightarrow Co(s) + Zn^{2+}(aq)$

$Mg^{2+}(aq) + Zn(s) \rightarrow$ no evidence of reaction

12. In a school laboratory, four metals were combined with each of four solutions and the following reactions occurred:

$Be(s) + Cd^{2+}(aq) \rightarrow Be^{2+}(aq) + Cd(s)$

$Cd(s) + 2\ H^+(aq) \rightarrow Cd^{2+}(aq) + H_2(g)$

$Ca^{2+}(aq) + Be(s) \rightarrow$ no evidence of reaction

$Cu(s) + H^+(aq) \rightarrow$ no evidence of reaction

Construct a table of relative strengths of oxidizing and reducing agents.

13. Is the redox spontaneity rule empirical or theoretical? Justify your answer.

14. Use the relative strengths of nonmetals and metals as oxidizing and reducing agents, as indicated in the following unbalanced equations, to construct a table of half-reactions.

$Ag(s) + Br_2(l) \rightarrow AgBr(s)$

$Ag(s) + I_2(s) \rightarrow$ no evidence of reaction

$Cu^{2+}(aq) + I^-(aq) \rightarrow$ no redox reaction

$Br_2(l) + Cl^-(aq) \rightarrow$ no evidence of reaction

Learning Tip

The nonspontaneity of a reaction is communicated in several ways: "no evidence of reaction," "nonspontaneous," "no reaction," or "nonspont," written over the equation arrow.

EXTENSION

Explaining Relative Strengths of Agents

Why are some metals more effective as reducing agents than others? The strength of a reducing agent depends on several factors. This audio clip provides a bit more background on what makes some metals stronger reducing agents than others.

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An Extended Redox Table

Chemists have analyzed evidence collected in many experiments, to produce an extended redox table of oxidizing and reducing agents, such as the one found in Appendix I. This table represents the combined efforts of many people over many years. A redox table is an important reference for chemists. You can use this table to compare oxidizing and reducing agents, and to predict spontaneous redox reactions.

Learning Tip

Although you can consult the redox table in Appendix I, it is much more efficient to memorize which classes of substances tend to be oxidizing agents or reducing agents (question 15). This general pattern helps to speed up the process of recognizing oxidizing and reducing agents and is necessary to classify substances that don't appear in Appendix I.

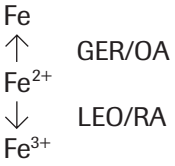

Figure 7
Iron(II) ions can either lose or gain electrons and, therefore, can act as either reducing agents or oxidizing agents.

DID YOU KNOW ?

Science and Belief Systems

Traditional knowledge of Aboriginal peoples is based on observation, experience, testing, teaching, and recording. Although the methodology may differ, this empirical basis is not that much different from Western science. Traditional knowledge, such as traditional ecological knowledge, is sometimes criticized within Western culture because of its connection to Aboriginal beliefs. Yet Western science also operates under a belief system that sometimes makes it difficult for novel ideas to become accepted. For example, Arrhenius' ideas were disputed and overruled by the prominent scientists of the day in spite of Arrhenius' solid evidence.

Practice

Use the redox table in Appendix I to answer the following questions.

15. Arrange the following metal ions in order of decreasing strength as oxidizing agents: lead(II) ions, silver ions, zinc ions, and copper(II) ions. How does this order compare with **Table 3** on page 570?

16. What classes of substances (e.g., metals, nonmetals, acidic, basic) usually behave as
(a) oxidizing agents? (b) reducing agents?

17. Use atomic theory to explain why nonmetals behave as oxidizing agents and metals behave as reducing agents. Is there logical consistency between atomic theory and the empirically determined table of oxidizing and reducing agents?

18. Trends in the reactivity of elements show that fluorine is the most reactive nonmetal. How does this relate to the position of fluorine in the redox table of oxidizing and reducing agents? State one reason why this element is the most reactive nonmetal. Why is your reason an explanation? (Keep asking a series of "why" questions until your theoretical knowledge is expended. Does your theory pass the test of being able to explain the empirically determined table?)

19. (a) Repeat your answer to question 16 using a Venn diagram (two large intersecting circles).
(b) Identify three oxidizing agents (other than $Fe^{2+}(aq)$, shown in **Figure 7**) from the redox table that can also act as reducing agents and record their symbols on your Venn diagram.
(c) Try to explain this surprising behaviour.

20. Use the redox spontaneity rule to predict whether the following mixtures will show evidence of a reaction; that is, predict whether the reactions are spontaneous. (Do not write the equations for the reaction.)
(a) nickel metal in a solution of silver ions
(b) zinc metal in a solution of aluminium ions
(c) an aqueous mixture of copper(II) ions and iodide ions
(d) chlorine gas bubbled into a bromide ion solution
(e) an aqueous mixture of copper(II) ions and tin(II) ions
(f) copper metal in nitric acid

21. Complete the Prediction, Design, and Materials (including safety precautions) for the following investigation.

Purpose
The purpose of this investigation is to test the order of strengths of oxidizing and reducing agents given on the redox table (Appendix I).

Problem
What is the relative order of strengths of oxidizing and reducing agents for aluminium, nickel, lead, cobalt, and their respective aqueous ions?

22. Describe two designs or methods that can be used to build a redox table.

23. From your knowledge, list two metals that are found as elements and two that are never found as elements in nature. Test your answer by referring to the position of these metals in the table of oxidizing and reducing agents.

24. Has empirical or theoretical knowledge been the most useful to you in predicting the spontaneity of redox reactions? Explain.

Predicting Redox Reactions in Solution

Arrhenius' ideas about solutions provide an important starting point for predicting redox reactions. In solutions, molecules and ions behave approximately independently of each other. A first step in predicting redox reactions is to list all entities that are present. (Some helpful reminders are listed in **Table 6**.) For example, when copper metal is placed into an acidic potassium permanganate solution, copper atoms, potassium ions, permanganate ions, hydrogen ions, and water molecules are all present. Next, using your knowledge of oxidizing and reducing agents, and the redox table in Appendix I, label all possible oxidizing and reducing agents in the starting mixture. The permanganate ion is listed as an oxidizing agent only in an acidic solution. To indicate this combination, draw an arc between the permanganate and hydrogen ions as shown below, and label the pair as an oxidizing agent. This procedure of listing and identifying entities present is a crucial step in predicting redox reactions.

	OA	OA	OA	OA
$Cu(s)$	$K^+(aq)$	$MnO_4^-(aq)$	$H^+(aq)$	$H_2O(l)$
RA				RA

Table 6 Hints for Listing and Labelling Entities

• Aqueous solutions contain $H_2O(l)$ molecules.
• Acidic solutions contain $H^+(aq)$ ions.
• Basic solutions contain $OH^-(aq)$ ions.
• Some oxidizing and reducing agents are combinations, for example, $MnO_4^-(aq)$ and $H^+(aq)$.
• $H_2O(l)$, $Fe^{2+}(aq)$, $Cu^+(aq)$, $Sn^{2+}(aq)$, and $Cr^{2+}(aq)$ may act as either oxidizing or reducing agents. Label both possibilities in your list.

Practice

25. List all entities initially present in the following mixtures, and identify all possible oxidizing and reducing agents.

(a) A lead strip is placed in a copper(II) sulfate solution.
(b) A gold coin is placed in a nitric acid solution.
(c) A potassium dichromate solution is added to an acidic iron(II) nitrate solution.
(d) An aqueous chlorine solution is added to a phosphorous acid solution.
(e) A potassium permanganate solution is mixed with an acidified tin(II) chloride solution.
(f) Iodine solution is added to a basic mixture containing manganese(IV) oxide.

We can use a redox table to identify the strongest oxidizing and reducing agents in a mixture, and then predict which reactions will occur. If we assume that collisions are completely random, the strongest oxidizing agent and the strongest reducing agent will react. (In some cases, further reactions may occur as well, but we will consider only the initial reaction, unless otherwise specified.) The following instructions allow you to make the correct and most efficient use of a redox table, such as the one in Appendix I.

- Choose the strongest oxidizing agent present in your mixture by starting at the top left corner of a redox table and going down the list until you find the oxidizing agent that is in your mixture.
- Choose the strongest reducing agent in your mixture by starting at the bottom right corner of the table and going up the list until you find the reducing agent that is in your mixture.
- Read reduction half-reaction equations from left to right (following the forward arrow).
- Read oxidation half-reaction equations from right to left (following the reverse arrow).
- Assume that any substances not present in the table are spectator ions. You do not need to label or consider these substances.

DID YOU KNOW?

Getting Rid of Skunk Odour

The smell of a skunk (**Figure 8**) is caused by a thiol compound (R–SH). To deodorize a pet sprayed by a skunk, you need to convert the smelly thiol to an odourless compound. Hydrogen peroxide in a basic solution (usually from sodium bicarbonate) acts as an oxidizing agent to change the thiol to a disulfide compound (RS–SR), which is odourless.

Figure 8
A skunk's only defence is its ability to spray a smelly liquid a distance of 3 m.

Learning Tip

- If the half-reaction equation shows two or more entities present, then both must be in your list. If there is only one entity, then leave it unlabelled as a spectator ion.
- Be careful with a few entities that can act either as an OA or an RA, for example, the iron(II) ion in Sample Problem 13.5.

Figure 9
A solution of potassium permanganate is being added to an acidic solution of iron(II) ions. The dark purple colour of $MnO_4^-(aq)$ ions instantly disappears. The interpretation is that $MnO_4^-(aq)$ ions react with $Fe^{2+}(aq)$ ions to produce the yellow-brown $Fe^{3+}(aq)$ and $Mn^{2+}(aq)$ ions.

SAMPLE problem 13.5

Suppose a solution of potassium permanganate is slowly poured into an acidified iron(II) sulfate solution. Does a redox reaction occur and, if it does, what is the reaction equation? Describe two diagnostic tests of your prediction.

To make a prediction, the entities initially present are identified as oxidizing agents, reducing agents, or both, as shown below.

OA	OA	OA	OA	OA	OA
$K^+(aq)$	$MnO_4^-(aq)$	$H^+(aq)$	$Fe^{2+}(aq)$	$SO_4^{2-}(aq)$	$H_2O(l)$
			RA		RA

Use the redox table in Appendix I to choose the strongest oxidizing agent and the strongest reducing agent from your list and indicate them as SOA and SRA.

OA	SOA	OA	OA	OA	OA
$K^+(aq)$	$MnO_4^-(aq)$	$H^+(aq)$	$Fe^{2+}(aq)$	$SO_4^{2-}(aq)$	$H_2O(l)$
			SRA		RA

Now, write the half-reaction equation for the reduction of the SOA from the redox table.

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Write the half-reaction equation for the oxidation of the SRA. Remember to read from right to left in the table.

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

Before combining the half-reaction equations, balance the number of electrons transferred by multiplying one or both half-reaction equations by an integer so that the number of electrons gained by the oxidizing agent equals the number of electrons lost by the reducing agent.

In this case, the iron ion half-reaction must be multiplied by 5. Add the two equations, but remember to cancel any common terms. You can cancel terms as you add (e.g., $5e^-$) or after you add the two half-reactions.

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$
$$5\,[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-\,]$$

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,Fe^{2+}(aq) \rightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

Finally, use the spontaneity rule to predict whether the net ionic equation represents a spontaneous redox reaction. Indicate this by writing "spont." or "nonspont." over the equation arrow.

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,Fe^{2+}(aq) \xrightarrow{\text{spont.}} 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

In this case, we predict that the reaction is spontaneous. We can test this prediction by mixing the solutions (**Figure 9**) and performing some diagnostic tests. If the solutions are mixed and the purple colour of the permanganate ion disappears, then it is likely that the permanganate ion reacted. If the pH of the solution is tested before and after reaction, and the pH has increased, then the hydrogen ions likely reacted.

COMMUNICATION example 1

In a chemical industry, could copper pipe be used to transport a hydrochloric acid solution? To answer this question,
(a) predict the redox reaction and its spontaneity, and
(b) describe two diagnostic tests that could be done to test your prediction.

Solution

(a)

SOA OA

$Cu(s)$ $H^+(aq)$ $Cl^-(aq)$ $H_2O(l)$

SRA RA RA RA

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$$
$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$$

$$2\,H^+(aq) + Cu(s) \xrightarrow{\text{nonspont.}} H_2(g) + Cu^{2+}(aq)$$

Since the reaction is nonspontaneous, it should be possible to use a copper pipe to carry hydrochloric acid.

(b) If no gas is produced when the mixture is observed, then it is likely that no hydrogen gas was produced (**Figure 10**). If the colour of the solution did not change to blue, then copper probably did not react to produce copper(II) ions. (If the solution is tested for pH before and after adding the copper, and the pH did not increase, then the hydrogen ions probably did not react.)

Figure 10
Copper in hydrochloric acid does not appear to react.

Disproportionation

Chemists believe that redox reactions are electron-transfer reactions. One reactant (OA) removes electrons from a second reactant (RA) if a spontaneous reaction takes place. Although the oxidizing and reducing agents that react are usually different entities, this is not a requirement. A reaction in which a species is both oxidized and reduced is called **disproportionation**. This type of reaction is often a redox reaction and occurs when a substance can act either as an oxidizing agent or as a reducing agent.

For example, we know that an iron(II) ion can behave either as an oxidizing agent or a reducing agent (**Figure 7**, page 574). What happens if two iron(II) ions in a solution collide? Will a spontaneous reaction occur as a result of an electron transfer from one iron(II) ion to another iron(II) ion?

$$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$$
$$2[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-]$$
$$3\,Fe^{2+}(aq) \rightarrow Fe(s) + 2\,Fe^{3+}(aq)$$

Using a redox table and the spontaneity rule with iron(II) as the strongest oxidizing agent and iron(II) as the strongest reducing agent, we see that this reaction is nonspontaneous.

Not all disproportionation reactions are nonspontaneous. For example, check the disproportionation of the copper(I) ion on the redox table in Appendix I. Copper(I) as an oxidizing agent appears above copper(I) as a reducing agent. Therefore, an aqueous solution of copper(I) ions will spontaneously, but slowly, disproportionate into copper(II) ions and copper metal.

Learning Tip

Disproportionation reactions are also referred to by the more descriptive terms of "self oxidation–reduction" or "autoxidation."

COMMUNICATION example 2

Will a solution of chromium(II) chloride be stable? Predict the redox reaction and its spontaneity.

Solution

SOA OA

$Cr^{2+}(aq)$ $Cl^{-}(aq)$ $H_2O(l)$

SRA RA RA RA

$$Cr^{2+}(aq) + 2\,e^{-} \rightarrow Cr(s)$$

$$2\,[Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + e^{-}]$$

$$3\,Cr^{2+}(aq) \xrightarrow{\text{nonspont.}} Cr(s) + 2\,Cr^{3+}(aq)$$

According to the redox table and the spontaneity rule, a chromium(II) chloride solution should not react and, therefore, should be stable.

SUMMARY Five-Step Method for Predicting Redox Reactions

Step 1: List all entities present and classify each as a possible oxidizing agent, reducing agent, or both. Do not label spectator ions.

Step 2: Choose the strongest oxidizing agent as indicated in a redox table, and write the equation for its reduction.

Step 3: Choose the strongest reducing agent as indicated in the table, and write the equation for its oxidation.

Step 4: Balance the number of electrons lost and gained in the half-reaction equations by multiplying one or both equations by a number. Then add the two balanced half-reaction equations to obtain a net ionic equation.

Step 5: Using the spontaneity rule, predict whether the net ionic equation represents a spontaneous or nonspontaneous redox reaction.

INVESTIGATION 13.3 *Introduction*

Predicting the Reaction of Sodium Metal (Demonstration)

The process of developing theories, laws, and generalizations requires that they be tested numerous times in as many different situations as possible. This process is necessary not only to determine their validity, but also to identify exceptions that may lead to new knowledge.

As part of the Design, include a list of diagnostic tests using the "If [procedure] and [evidence], then [analysis]" format for every product predicted. (This format is described in Appendix C.4.)

To perform this investigation, turn to page 602.

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	○ Materials	● Evaluation (1, 2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Purpose

The purpose of this demonstration is to test the five-step method for predicting redox reactions.

Problem

What are the products of the reaction of sodium metal with water?

Practice

26. Use the five-step method to predict the most likely redox reaction in each of the following situations. For any spontaneous reaction, describe one diagnostic test to identify a primary product.
(a) During a demonstration, zinc metal is placed in a hydrochloric acid solution.
(b) A gold ring accidentally falls into a hydrochloric acid solution.
(c) Nitric acid is painted onto a copper sheet to etch a design.

27. In your previous chemistry course, you made predictions of reactions according to the single replacement generalization assuming the formation of the most common ion.
(a) Use the generalization about single replacement reactions to predict the reaction of iron metal with a copper(II) sulfate solution.
(b) Use the redox theory and table to predict the most likely redox reaction of iron metal with a copper(II) sulfate solution.
(c) Can both predictions be correct? Which do you think is most likely correct and why?
(d) Write one qualitative and one quantitative experimental design to test the two different predictions made for the reaction between iron metal and the copper(II) sulfate solution.

28. Write a Prediction, with your reasoning, and a Design (including safety precautions, diagnostic tests, and disposal instructions) for the following experiment.

Problem
What are the products of the reaction of tin(II) chloride with an ammonium dichromate solution acidified with hydrochloric acid?

29. When aluminium pots are used for cooking, small pits often develop in the metal. Use your knowledge of redox reactions to explain the formation of these pits. Suggest why this might be a slow process.

30. Oxygen gas is bubbled into an aqueous solution of iron(II) iodide containing excess hydrochloric acid. Predict all spontaneous reactions in the order in which they will occur.

DID YOU KNOW ?

Aluminium Oxide Clouds

The solid rocket boosters of the space shuttle contain the main reactants ammonium perchlorate and aluminium powder. Ammonium perchlorate is a powerful oxidizing agent and aluminium is a relatively strong reducing agent. Their very exothermic reaction produces finely divided aluminium oxide, which forms the billows of white smoke you see in **Figure 11**.

Figure 11
The space shuttle

Predicting Redox Reactions by Constructing Half-Reactions

A redox reaction includes both an oxidation and a reduction. In other words, one substance has to lose electrons as another substance gains electrons. Choosing and writing half-reaction equations is commonly done using a table of relative strengths of oxidizing and reducing agents. But what if this table does not provide the half-reaction equations needed? In this case, use your knowledge about constructing your own half-reaction equations (refer to the Summary on page 567), and then balance electrons to obtain the overall redox reaction equation.

For a particular reaction, chemists know the main starting materials and the reaction conditions (such as acidic or basic). A chemical analysis of the products determines the oxidized and reduced species produced in the reaction. This provides a *skeleton equation* showing only the main reactants and products. Chemists can then determine the details of the final redox equation by looking at the individual balanced half-reaction equations.

Figure 12
A breathalyzer is a technological device that measures the alcohol content in exhaled air based on the colour change from orange (dichromate ion) to green (chromium(III) ion) when an acidic dichromate ion solution reacts with ethanol in a breath sample.

SAMPLE problem 13.6

A common example of the application of redox reactions is the technology of a breathalyzer (**Figure 12**). A person suspected of being intoxicated blows into this device and the alcohol in the person's breath reacts with an acidic dichromate ion solution to produce acetic acid (ethanoic acid) and aqueous chromium(III) ions. Predict the balanced redox reaction equation.

The information provided tells you the skeleton equation for the major reactants and products.

$$C_2H_5OH(aq) + Cr_2O_7^{2-}(aq) \rightarrow CH_3COOH(aq) + Cr^{3+}(aq)$$

The first step is to separate the entities into the start of two half-reaction equations, keeping related entities together.

$$C_2H_5OH(aq) \rightarrow CH_3COOH(aq)$$

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

Now you can complete each half-reaction equation using the same procedure you used in Section 13.1: Balance atoms other than O and H; balance O by adding $H_2O(l)$; balance H by adding $H^+(aq)$; and finally balance the charge by adding electrons. For the ethanol half-reaction,

$$H_2O(l) + C_2H_5OH(aq) \rightarrow CH_3COOH(aq) + 4\ H^+(aq) + 4\ e^-$$

Follow the same procedure to construct the second half-reaction equation.

$$6\ e^- + 14\ H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$$

Recall that the total number of electrons lost must equal the total number of electrons gained. Using the simplest whole numbers, multiply one or both half-reaction equations so that the electrons will be balanced. In this example, the simplest solution is a total of twelve electrons transferred.

$$3\ [H_2O(l) + C_2H_5OH(aq) \rightarrow CH_3COOH(aq) + 4\ H^+(aq) + 4\ e^-]$$

$$2\ [6\ e^- + 14\ H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)]$$

Add the two half-reaction equations. Cancel the electrons and anything else that is the same on both sides of the equation. Note that it is not unusual to have unequal chemical amounts of some entities, such as hydrogen ions and water, on the two sides of the equations. The lower amount will always cancel completely. For example, 3 $H_2O(l)$ from the first half-reaction equation cancels 3 mol out of the 14 $H_2O(l)$ in the second equation leaving 11 $H_2O(l)$ in the net equation.

$$3\ C_2H_5OH(aq) + 2\ Cr_2O_7^{2-}(aq) + 16\ H^+(aq) \rightarrow 3\ CH_3COOH(aq) + 4\ Cr^{3+}(aq) + 11\ H_2O(l)$$

Check the final redox equation to make sure that both the symbols and the charges are balanced.

For reactions that occur in basic solutions, you can follow the procedure outlined in Sample Problem 13.6, and then convert to a basic solution. In other words, create the balanced redox equation for an acidic solution, and then add $OH^-(aq)$ to convert the $H^+(aq)$ to water molecules. An example for a basic solution is shown in the following Communication Example.

CAREER CONNECTION

Conservator

The career of conservator is highly varied, allowing these professionals to tailor their work to their own special interests. Conservators work with a wide range of objects, including antique metals, furniture, and ceramics. The conservator makes recommendations on how the objects should be preserved, as well as performs chemical analyses to treat existing damage. Conservators often use chemistry to restore historical artifacts. Find out more about the requirements for this interesting and challenging career.

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COMMUNICATION example 3

Permanganate ions and oxalate ions react in a basic solution to produce carbon dioxide and manganese(IV) oxide.

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow CO_2(g) + MnO_2(s)$$

Write the balanced redox equation for this reaction.

Solution

$$2\,[3\,e^- + 4\,H^+(aq) + MnO_4^-(aq) \rightarrow MnO_2(s) + 2\,H_2O(l)]$$
$$3\,[C_2O_4^{2-}(aq) \rightarrow 2\,CO_2(g) + 2\,e^-]$$

$$8\,H^+(aq) + 2\,MnO_4^-(aq) + 3\,C_2O_4^{2-}(aq) \rightarrow 2\,MnO_2(s) + 4\,H_2O(l) + 6\,CO_2(g)$$

$$8\,OH^-(aq) + 8\,H^+(aq) + 2\,MnO_4^-(aq) + 3\,C_2O_4^{2-}(aq) \rightarrow 2\,MnO_2(s) + 4\,H_2O(l) + 6\,CO_2(g) + 8\,OH^-(aq)$$

$$4\,H_2O(l) + 2\,MnO_4^-(aq) + 3\,C_2O_4^{2-}(aq) \rightarrow 2\,MnO_2(s) + 6\,CO_2(g) + 8\,OH^-(aq)$$

Learning Tip

Always check your final answer by counting the number of each kind of atom on both sides of the equation, and by checking the net charge on each side.

Practice

31. Balance the following redox equations using the half-reaction method. All reactions occur in an acidic solution.

(a) $Zn(s) + NO_3^-(aq) \rightarrow NH_4^+(aq) + Zn^{2+}(aq)$

(b) $Cl_2(aq) + SO_2(g) \rightarrow Cl^-(aq) + SO_4^{2-}(aq)$

32. Balance the following skeleton redox equations using the half-reaction method. All reactions occur in a basic solution.

(a) $MnO_4^-(aq) + I^-(aq) \rightarrow MnO_2(s) + I_2(s)$

(b) $CN^-(aq) + IO_3^-(aq) \rightarrow CNO^-(aq) + I^-(aq)$

(c) $OCl^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$

33. Balance the following redox equation.

$$KMnO_4(aq) + H_2S(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + MnSO_4(aq) + S(s)$$

SUMMARY Predicting Balanced Redox Equations by Constructing Half-Reactions

Step 1: Use the information provided to start two half-reaction equations.
Step 2: Balance each half-reaction equation.
Step 3: Multiply each half-reaction equation by simple whole numbers to balance the electrons lost and gained.
Step 4: Add the two half-reaction equations, cancelling the electrons and anything else that is exactly the same on both sides of the equation.

For basic solutions only

Step 5: Add $OH^-(aq)$ to both sides equal in number to the number of $H^+(aq)$ present.
Step 6: Combine $H^+(aq)$ and $OH^-(aq)$ on the same side to form $H_2O(l)$, and cancel the same number of $H_2O(l)$ on both sides.

Section 13.2 Questions

1. What is the key idea used to explain a redox reaction?
2. Distinguish between oxidation and oxidizing agent in terms of modern theory.
3. Distinguish between reduction and reducing agent in terms of modern theory.
4. Write and label two half-reaction equations to describe each of the following reactions:
   (a) $Co(s) + Cu(NO_3)_2(aq) \rightarrow Cu(s) + Co(NO_3)_2(aq)$
   (b) $Cd(s) + Zn(NO_3)_2(aq) \rightarrow Zn(s) + Cd(NO_3)_2(aq)$
   (c) $Br_2(l) + 2\,KI(aq) \rightarrow I_2(s) + 2\,KBr(aq)$
5. Using the redox table in Appendix I, predict the spontaneity of each of the reactions shown in 4(a) to (c).
6. Prepare a redox table showing the relative strengths of oxidizing and reducing agents in **Table 7**.

Table 7 Reactions of Group 13 Elements and Ions

	$Al^{3+}(aq)$	$Tl^{+}(aq)$	$Ga^{3+}(aq)$	$In^{3+}(aq)$
Al	X	✓	✓	✓
Tl	X	X	X	X
Ga	X	✓	X	✓
In	X	✓	X	X

X no evidence of a redox reaction ✓ a spontaneous reaction

7. What is the relative strength of oxidizing and reducing agents for strontium, cerium, nickel, hydrogen, platinum, and their aqueous ions? Use the following information to construct a table of relative strengths of oxidizing and reducing agents.
   $3\,Sr(s) + 2\,Ce^{3+}(aq) \rightarrow 3\,Sr^{2+}(aq) + 2\,Ce(s)$
   $Ni(s) + 2\,H^{+}(aq) \rightarrow Ni^{2+}(aq) + H_2(g)$
   $2\,Ce^{3+}(aq) + 3\,Ni(s) \rightarrow$ no evidence of reaction
   $Pt(s) + 2\,H^{+}(aq) \rightarrow$ no evidence of reaction
8. Write an experimental design to determine a mini-redox table for the first three metals and metal ions of Group 12. Include safety and disposal information.
9. For each of the following mixtures, use the complete five-step method to predict the most likely redox reaction. Include one diagnostic test to test your predicted reaction.
   (a) Solutions of nickel(II) nitrate and iron(II) chloride are mixed.
   (b) Oxygen gas is bubbled over a solid silver mesh immersed in a solution of sodium iodide.
   (c) An acidic solution of potassium dichromate is added to a sodium iodide solution.
10. A chemical technician prepares several solutions for use in a chemical analysis. Will each of the solutions listed below be stable if stored for a long time? Justify your answer.
    (a) acidic tin(II) chloride in an inert glass container
    (b) copper(II) nitrate in a tin can
11. In the industrial production of iodine, chlorine gas is bubbled into seawater. Using only water and iodide ions in seawater as the possible reactants, predict the most likely redox reaction, including equations for the half-reactions.
12. The steel of an automobile fender is exposed to acid rain. (Assume that steel is made mainly of iron.) Predict the most likely redox reactions, including the equations for the relevant half-reactions.
13. Define disproportionation and illustrate it using half-reaction equations of tin(II) ions.
14. An excess of cobalt metal was left in an aqueous mixture containing silver ions, iron(III) ions, and copper(II) ions for an extended time. Write a balanced redox equation for every reaction that occurs.
15. Balance the following equation representing a reaction that occurs in an acidic solution:
    $Mn^{2+}(aq) + HBiO_3(aq) \rightarrow Bi^{3+}(aq) + MnO_4^{-}(aq)$
16. Balance the following equations representing reactions that occur in a basic solution:
    (a) $Cr(OH)_3(s) + IO_3^{-}(aq) \rightarrow CrO_4^{2-}(aq) + I^{-}(aq)$
    (b) $Ag_2O(s) + CH_2O(aq) \rightarrow Ag(s) + CHO_2^{-}(aq)$
17. Many commercially available drain cleaners contain a basic solution of sodium hydroxide, which helps to remove grease in the drains. Some solid drain cleaners contain solid sodium hydroxide and finely divided aluminium metal. When mixed with water, this produces a very vigorous, exothermic reaction shown by the following skeleton equation:
    $Al(s) + H_2O(l) \rightarrow Al(OH)_4^{-}(aq) + H_2(g)$
    (a) Complete the balanced redox equation for this reaction.
    (b) How does this chemical technology provide a solution to a practical problem?
    (c) Describe and discuss some possible health and safety issues associated with the use of solid drain cleaners.
18. What is the WHMIS symbol for oxidizing materials? What Household Hazardous Product Symbols would be used for oxidizing materials present in a consumer product?

Extension

19. The subject of antioxidants may be controversial, but there are many groups and companies that want you to use antioxidant products. What does the term *antioxidant* suggest? Define antioxidant and list three important examples. Briefly summarize some of the controversy that is associated with antioxidants.

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20. Many biologically important molecules contain a metal ion surrounded by and bonded to a large organic molecule (such as porphyrin). One very important example is chlorophyll. Prepare a report (paper, poster, or electronic) that contains information about the structure of the main form of chlorophyll, the general role that chlorophyll plays in electron transfer reactions, the close relatives of chlorophyll that contain iron and cobalt, and a technological application inspired by the chlorophyll molecule.

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Oxidation States 13.3

Historically, oxidation and reduction were considered to be separate processes, more of interest for technology than for science. With modern atomic theory came the idea of an electron transfer involving both a gain of electrons by one entity and a loss of electrons by another entity. This theory of redox reactions is most easily understood for atoms or monatomic ions. Metals and monatomic anions tend to lose electrons (become oxidized), whereas nonmetals and monatomic cations tend to gain electrons (become reduced).

More complex redox reactions, such as the reduction of iron(III) oxide by carbon monoxide in iron production, the oxidation of glucose in cellular respiration, and the use of dichromate ions in chemical analysis, are not adequately described or explained with simple redox theory.

To describe the oxidation and reduction of molecules and polyatomic ions, chemists developed a method of "electron bookkeeping" to keep track of the loss and gain of electrons. The idea is similar to determining the electric charge of a simple ion by counting electrons and protons; for example, a sodium ion ($11p^+$, $10e^-$) has an ion charge of $1+$. For atoms in molecules and polyatomic ions, chemists count a shared pair of electrons in a covalent bond as if it belongs entirely to the more electronegative atom in the bond. For example, in a water molecule (**Figure 1**), the shared pairs of electrons are assigned to the oxygen atom because oxygen has a higher electronegativity (3.5) compared with hydrogen (2.1). Now we can count the electrons around the oxygen and compare this with the number of protons in the nucleus (just like we do for simple ions). In this system, the *oxidation state* of an atom in an entity is defined as the apparent net electric charge that an atom would have if electron pairs in covalent bonds belonged entirely to the more electronegative atom. An oxidation state is a useful idea for keeping track of electrons, but it does not represent an actual charge on an atom—oxidation states are arbitrary charges and should not be confused with actual electric charges.

An **oxidation number** is a positive or negative number corresponding to the oxidation state assigned to an atom in a covalently bonded entity. For example, in a water molecule, the oxidation number of the oxygen atom is -2 and the oxidation number of each hydrogen atom is $+1$.

To distinguish oxidation numbers from actual electrical charges, oxidation numbers are written in this textbook as positive or negative numbers; that is, with the sign preceding the number. Chemists use this method to assign oxidation numbers to many common atoms and ions (**Table 1**), which can then be used to determine the oxidation numbers of other atoms.

Table 1 Common Oxidation Numbers

Atom or ion	Oxidation number	Examples
all atoms in elements	0	Na is 0 Cl in Cl_2 is 0
hydrogen in all compounds, except hydrogen in hydrides	$+1$ -1	H in HCl is $+1$ H in LiH is -1
oxygen in all compounds, except oxygen in peroxides	-2 -1	O in H_2O is -2 O in H_2O_2 is -1
all monatomic ions	charge on ion	Na^+ is $+1$ S^{2-} is -2

Learning Tip

Although the meaning of the terms *oxidation state* and *oxidation number* are slightly different, some people use these terms interchangeably.

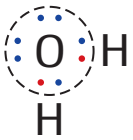


Figure 1
An oxygen atom has $8\,p^+$ and $8\,e^-$. If the oxygen atom gets to count the two hydrogen electrons in the two shared pairs of electrons, then $8\,p^+$ and $10\,e^-$ results in an apparent net charge of $2-$. Each hydrogen atom with $1\,p^+$ has no additional electrons. Its one electron has already been counted by the oxygen atom. Therefore, the hydrogen has an apparent net charge of $1+$.

Learning Tip

Oxidation numbers are simply positive or negative numbers assigned on the basis of a set of arbitrary rules. It is important for you to realize that these are not electric charges. For this reason, chemists use the term *oxidation number*. For example, we assign oxidation numbers of -2 and $+1$ to the oxygen and hydrogen atoms in a water molecule.

Oxidation numbers are simply a systematic way of counting electrons. Therefore, the sum of the oxidation numbers in a compound or ion must equal the total charge—zero for neutral compounds and the ion charge for ions.

Learning Tip

1. The sum of the oxidation numbers of any entity must equal the net charge on that entity: zero for neutral compounds, the ion charge for polyatomic ions.
2. The method only works if there is just one unknown after referring to **Table 1**. If there are two or more unknowns, a Lewis formula and electronegativities are required.

SAMPLE problem 13.7

What is the oxidation number of carbon in methane, CH_4?

This is determined by assigning an oxidation number of $+1$ to hydrogen (**Table 1**).

$$\overset{x}{C}\overset{+1}{H_4}$$

Now solve for x. Since a methane molecule is electrically neutral, the oxidation numbers of the one carbon atom and the four hydrogen atoms (4 times $+1$) must equal zero.

$$x + 4(+1) = 0$$
$$x = -4$$

$\overset{x}{C}\overset{+1}{H_4}$ becomes $\overset{-4}{C}\overset{+1}{H_4}$

Carbon in methane has an oxidation number of -4.

SAMPLE problem 13.8

What is the oxidation number of manganese in a permanganate ion, MnO_4^-.

The oxidation number of manganese in the permanganate ion, MnO_4^-, is determined using the oxidation number of oxygen as -2 (**Table 1**) and the knowledge that the charge on the ion is $1-$. The total of the oxidation numbers of the one manganese atom (x) and the four oxygen atoms (4 times -2) must equal the charge on the ion ($1-$).

$$x + 4(-2) = -1$$
$$x = +7$$

$\overset{x}{Mn}\overset{-2}{O_4^-}$ becomes $\overset{+7}{Mn}\overset{-2}{O_4^-}$

The oxidation number of manganese in MnO_4^- is $+7$.

Learning Tip

Alternatively, you can always split an ionic formula into the cation and anion before solving for an unknown oxidation number.

For example, if you want to know the oxidation number for sulfur in sodium sulfate, start with the sulfate ion:

$$\overset{x}{S}\overset{-2}{O_4^{2-}}$$

$x + 4(-2) = -2 \qquad x = +6$

COMMUNICATION example 1

What is the oxidation number of sulfur in sodium sulfate?

Solution

$\overset{+1}{Na_2}\overset{x}{S}\overset{-2}{O_4}$ $\qquad 2(+1) + x + 4(-2) = 0$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad x = +6$

According to the concept of oxidation states, the oxidation number of sulfur in sodium sulfate is $+6$.

SUMMARY Determining Oxidation Numbers

Step 1: Assign common oxidation numbers (**Table 1** on page 583).

Step 2: The total of the oxidation numbers of atoms in a molecule or ion equals the value of the net electric charge on the molecule or ion.

(a) The sum of the oxidation numbers for a compound is zero.

(b) The sum of the oxidation numbers for a polyatomic ion equals the charge on the ion.

Step 3: Any unknown oxidation number is determined algebraically from the sum of the known oxidation numbers and the net charge on the entity.

Practice

1. Determine the oxidation number of

(a) S in SO_2 (c) S in SO_4^{2-} (e) I in MgI_2

(b) Cl in $HClO_4$ (d) Cr in $Cr_2O_7^{2-}$ (f) H in CaH_2

2. Determine the oxidation number of nitrogen in

(a) $N_2O(g)$ (d) $NH_3(g)$ (g) $N_2(g)$

(b) $NO(g)$ (e) $N_2H_4(g)$ (h) $NH_4Cl(s)$

(c) $NO_2(g)$ (f) $NaNO_3(s)$

3. Determine the oxidation number of carbon in

(a) graphite (elemental carbon) (c) sodium carbonate

(b) glucose (d) carbon monoxide

4. Bruderheim, Alberta, is the site of several companies that produce sodium chlorate. Almost all of the sodium chlorate produced is sold to pulp and paper mills to produce chlorine dioxide as a bleaching agent (**Figure 2**). Determine the oxidation number of every atom or ion in the following chemical equation for the industrial production of chlorine dioxide.

$$2\,ClO_3^-(aq) + 2\,Cl^-(aq) + 4\,H^+(aq) \rightarrow 2\,ClO_2(g) + Cl_2(g) + 2\,H_2O(l)$$

5. Carbon can be progressively oxidized in a series of organic reactions. Determine the oxidation number of carbon in each of the compounds in the following series of oxidations:

methane →	methanol →	methanal →	methanoic acid →	carbon dioxide
CH_4	CH_3OH	CH_2O	HCOOH	CO_2

Figure 2
The bleaching of wood pulp to produce white paper is now mostly done using chlorine dioxide in place of the more environmentally damaging elemental chlorine.

Oxidation Numbers and Redox Reactions

Although the concept of oxidation states is somewhat arbitrary, because it is based on assigned charges, it is self-consistent and allows predictions of electron transfer. Chemists believe that if the oxidation number of an atom or ion changes during a chemical reaction, then an electron transfer (that is, an oxidation–reduction reaction) occurs. Based on oxidation numbers, an increase in the oxidation number is defined as an **oxidation** and a decrease in the oxidation number is a **reduction**. If oxidation numbers are listed as positive and negative numbers on a number line (**Figure 3**), then the process of oxidation involves a change to a more positive value ("up" on the number line) and reduction is a change to a more negative value ("down" on the number line). If the oxidation numbers do not change, this is interpreted as no transfer of electrons. A reaction in which all oxidation numbers remain the same is not a redox reaction.

Coal is a fossil fuel that is burned in huge quantities in some electrical power generating stations. If we assume pure carbon and complete combustion, carbon is converted to carbon dioxide. In this reaction, the oxidation number of carbon changes from 0 in

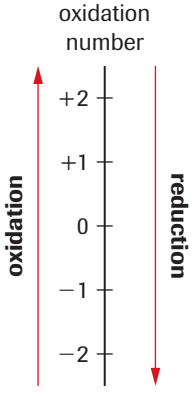
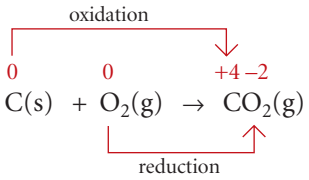


Figure 3
In a redox reaction, both oxidation and reduction occur.

C(s) to +4 in $CO_2(g)$. Simultaneously, oxygen is reduced from 0 in $O_2(g)$ to −2 in $CO_2(g)$.



The main purpose of assigning oxidation numbers is to see how these numbers change as a result of a chemical reaction. In any redox reaction, like the combustion of carbon, there will always be both an oxidation and a reduction. We will use these changes to balance redox equations, but first we will look at some additional examples.

LAB EXERCISE 13.B

Oxidation States of Vanadium

Vanadium is a transition metal that forms many different ions (**Table 2**). Vanadium and its compounds have many different uses, including colouring for glass, ceramics, and plastics.

Purpose

The purpose of this lab exercise is to use the concept of oxidation states to investigate some redox chemistry of vanadium compounds.

Problem

What are the oxidation numbers and changes in oxidation number for vanadium ions?

Table 2 Colours of Vanadium Ions

Ion name	Ion formula	Colour
vanadate(V)	$VO_3^-(aq)$	
vanadate (IV)	$VO^{2+}(aq)$	
vanadium(III)	$V^{3+}(aq)$	
vanadium(II)	$V^{2+}(aq)$	

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ○ Evidence
- ● Analysis
- ○ Evaluation

Analysis

(a) Using **Table 2**, identify the vanadium ions in the sequence of reactions in **Table 3**.
(b) In each case, is the vanadium being oxidized or reduced? Justify your answer, using oxidation numbers.
(c) Explain the observations made in (3) to (6) in **Table 3**. Suggest what is causing these changes.

Evidence

Table 3 Reactions of Vanadium Ions

Procedure	Final solution colours
(1) ammonium vanadate(V) dissolved in sulfuric acid	yellow
(2) yellow solution with three subsequent additions of small quantities of zinc dust	yellow turned blue, then green, then violet
(3) violet solution left sitting in an open container	slowly turned green
(4) yellow solution mixed with potassium iodide solution	very dark blue, almost black
(5) blue solution mixed with potassium iodide solution	stayed blue; no change
(6) violet solution slowly mixed with acidic potassium permanganate	violet to green to blue to yellow

SAMPLE problem 13.9

You have seen the reaction of active metals such as zinc with an acid. Identify the oxidation and reduction in the reaction of zinc metal with hydrochloric acid.

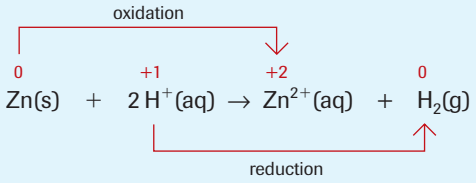
First, you need to write the chemical equation, as it is not provided. Net ionic equations are best, but the procedure will still work if you write a nonionic equation.

$$Zn(s) + 2\,H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

After writing the equation, determine all oxidation numbers.

$$\overset{0}{Zn}(s) + 2\,\overset{+1}{H^+}(aq) \rightarrow \overset{+2}{Zn^{2+}}(aq) + \overset{0}{H_2}(g)$$

Now look for the oxidation number of an atom/ion that increases as a result of the reaction and label the change as oxidation. There must also be an atom/ion whose oxidation number decreases. Label this change as reduction.



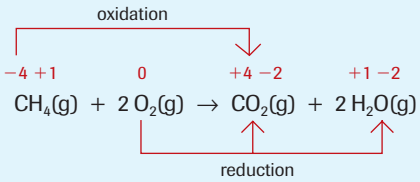
SAMPLE problem 13.10

When natural gas burns in a furnace, carbon dioxide and water form. Identify oxidation and reduction in this reaction.

First, write the equation.

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$$

Now we can insert the oxidation numbers and arrows.



Carbon is oxidized from -4 in methane to $+4$ in carbon dioxide as it reacts with oxygen. Simultaneously, oxygen is reduced from 0 in oxygen gas to -2 in both products.

Notice that the oxygen atoms in the reactant are distributed between the two products. This does not change our procedure because we are only looking for the change from reactant to product. We say that "oxygen is reduced" in this reaction and it does not matter where the reduced oxygen appears in the products.

DID YOU KNOW ?

Redox in Biological Systems

Biologists often classify oxidation and reduction in terms of the addition or removal of oxygen or hydrogen.

- Removal of oxygen decreases the oxidation number of carbon (i.e., a reduction), e.g.,

  $HCOOH \rightarrow HCHO$

  C is $+2$ C is 0

  The reverse also applies. Addition of oxygen corresponds to an oxidation.

- Removal of hydrogen increases the oxidation number of carbon (i.e., an oxidation), e.g., in the nicotinamide coenzyme

  $NADH \rightarrow NAD^+$

  C is $+2$ C is -1

  The reverse also applies. Addition of hydrogen corresponds to a reduction.

DID YOU KNOW?

Redox Reactions in Living Organisms

The ability of carbon to take on different oxidation states is essential to life on Earth. Photosynthesis involves a series of reduction reactions in which the oxidation number of carbon changes from +4 in carbon dioxide to an average of 0 in sugars such as glucose.

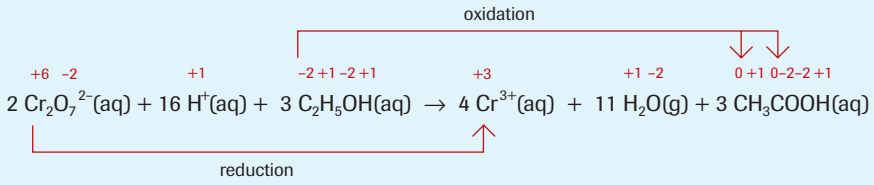
Silicon, which resembles carbon, has been postulated as a foundation for life elsewhere in the universe. The most common oxidation number for silicon is +4.

COMMUNICATION example 2

The determination of blood alcohol content from a sample of breath (**Figure 12**, page 580) or blood involves the reaction of the sample with acidic potassium dichromate solution. If ethanol is present, chromium(III) ions, water, and acetic acid are produced. Identify the oxidation and reduction in the following chemical reaction:

$$2\ Cr_2O_7^{2-}(aq) + 16\ H^+(aq) + 3\ C_2H_5OH(aq) \rightarrow 4\ Cr^{3+}(aq) + 11\ H_2O(g) + 3\ CH_3COOH(aq)$$

Solution



According to the concept of oxidation states, chromium atoms in $Cr_2O_7^{2-}$ are reduced (+6 to +3). Carbon atoms in C_2H_5OH are oxidized (−2 to 0).

SUMMARY Electron Transfer and Oxidation States

- According to current theory, a redox reaction is a chemical reaction in which electrons are transferred and the oxidation numbers change.
- Oxidation is the increase in oxidation number and corresponds to a loss of electrons.
- Reduction is the decrease in oxidation number and corresponds to a gain of electrons.

WWW WEB Activity

Case Study—Catalytic Converters

The catalytic converter is a technological development designed to reduce the amount of pollutants in an automobile's exhaust. Describe the main components of the converter and explain the three main reactions. Use oxidation numbers in your explanation.

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Practice

6. Methanol reacts with acidic permanganate ions as shown below:

$$5\ CH_3OH(l) + 2\ MnO_4^-(aq) + 6\ H^+(aq) \rightarrow 5\ CH_2O(l) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$$

(a) Assign oxidation numbers to all atoms/ions.
(b) Which atom/ion is oxidized? Label the oxidation above the equation.
(c) Which atom/ion is reduced? Label the reduction below the equation.

7. For each of the following chemical reactions, assign oxidation numbers to each atom/ion and indicate whether the equation represents a redox reaction. If it does, identify the oxidation and reduction.
   (a) $Cu(s) + 2\,AgNO_3(aq) \rightarrow 2\,Ag(s) + Cu(NO_3)_2(aq)$
   (b) $Pb(NO_3)_2(aq) + 2\,KI(aq) \rightarrow PbI_2(s) + 2\,KNO_3(aq)$
   (c) $Cl_2(aq) + 2\,KI(aq) \rightarrow I_2(s) + 2\,KCl(aq)$
   (d) $2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)$
   (e) $HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$
   (f) $2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)$
   (g) $2\,C_4H_{10}(g) + 13\,O_2(g) \rightarrow 8\,CO_2(g) + 10\,H_2O(l)$
   (h) $2\,H_2O_2(l) \rightarrow 2\,H_2O(l) + O_2(g)$
8. Where possible, classify the chemical equations in question 7 (a–h) using the five reaction types: formation, simple decomposition, single replacement, double replacement, and complete combustion. Which reaction type does not appear to be a redox reaction?
9. Hydrogen peroxide, $H_2O_2(l)$, can either be oxidized or reduced depending on the substance with which it reacts. Use oxidation numbers to explain why this is possible.
10. Earth has an oxidizing atmosphere of oxygen. The planet Saturn has a reducing atmosphere of hydrogen and methane. Describe the two types of atmospheres in terms of changes in oxidation numbers of carbon and of the likely reactions.

Balancing Redox Equations Using Oxidation Numbers

Knowing the ratio of reacting chemicals is necessary in many applications. Chemists use the mole ratio from a balanced chemical equation to study the nature of the reaction. The stoichiometry of a reaction is essential in many types of chemical analysis, such as the breathalyzer. Finally, chemical industries need to know the quantities of reactants to mix and the yield of a desired product. In this and previous courses, you have already seen many examples of the use of balanced chemical equations.

Simple redox reaction equations can be balanced by inspection or by a trial-and-error method. You have done this often in previous courses for reactions such as single replacement and combustion. More complex redox reactions may be very difficult to balance this way because of the number and complexity of the reactants and products. As you will see, oxidation numbers and half-reaction equations can be used to balance any redox equation.

One way of recognizing a redox reaction is to assign oxidation numbers to each atom or ion, and then look for any changes in the numbers. Any change in the oxidation number of a particular atom or ion is believed to be related to a change in the number of electrons. Because electrons are transferred in a redox reaction, the total number of electrons lost by one atom/ion must equal the total number of electrons gained by another atom/ion. In terms of oxidation numbers, this means that the changes in oxidation numbers must also be balanced.

The total increase in oxidation number for a particular atom/ion must equal the total decrease in oxidation number of another atom/ion.

Let's look at a simple example first. You could easily balance this equation by inspection, but we will use it to illustrate the main points of the oxidation number method.

Learning Tip

All redox reactions are electron transfer reactions. This means that the electrons that are lost by one entity are the same electrons that are gained by another. This is like you giving five dollars to a friend. You lose five dollars and your friend gains five dollars: five dollars has been transferred. Obviously, the money lost must equal the money gained. The same is true for electrons in a redox reaction.

Figure 4
Since sour natural gas often contains hydrogen sulfide, burning it can be a significant source of pollutants. It is also a waste of energy when many of these flares operate in a large oil field.

Learning Tip

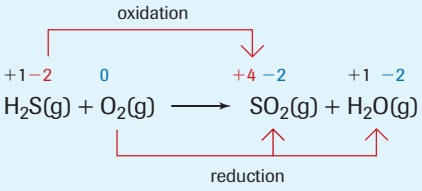
You can adjust the number of electrons per atom to the number per molecule by multiplying the number per atom by the subscript of the atom in the chemical formula.

SAMPLE problem 13.11

Hydrogen sulfide is an unpleasant constituent of "sour" natural gas. Hydrogen sulfide is not only very toxic, but it also smells terrible, similar to rotting eggs. It is common practice to "flare," or burn, relatively small quantities of sour natural gas that occur with oil deposits (**Figure 4**). The gas is burned because it is not worth recovering and treating a small quantity of gas. When this gas is burned, hydrogen sulfide is converted to sulfur dioxide. Use oxidation numbers to balance this equation.

$$H_2S(g) + O_2(g) \rightarrow SO_2(g) + H_2O(g)$$

The first step is to assign oxidation numbers to all atoms/ions and look for the numbers that change. Circle or highlight the oxidation numbers that change.



Notice that a sulfur atom is oxidized from −2 to +4. This is a change of 6 and means 6 e^- have been transferred. An oxygen atom is reduced from 0 to −2, a change of 2 or 2 e^- transferred. Because the substances in the equation are molecules, not atoms, we need to specify the change in the number of electrons per molecule.

$^{+1\ -2}$		^{0}		$^{+4\ -2}$		$^{+1\ -2}$
$H_2S(g)$	+	$O_2(g)$	→	$SO_2(g)$	+	$H_2O(g)$
6 e^-/S atom		2 e^-/O atom				
6 e^-/H_2S		4 e^-/O_2				

One H_2S molecule contains one sulfur atom. Therefore, the number of electrons transferred per sulfur atom is the same number per H_2S molecule. An O_2 molecule contains two O atoms. Therefore, when one O_2 molecule reacts, two oxygen atoms transfer 2 e^- each for a total of 4 e^-.

The next step is to determine the simplest whole numbers that will balance the number of electrons transferred for each reactant. The numbers become the coefficients for the reactants.

$^{+1\ -2}$		^{0}		$^{+4\ -2}$		$^{+1\ -2}$
$H_2S(g)$	+	$O_2(g)$	→	$SO_2(g)$	+	$H_2O(g)$
6 e^-/S atom		2 e^-/O atom				
6 e^-/H_2S		4 e^-/O_2				
× **2**		× **3**				
12		12				

Now you have the coefficients for the reactants.

$$\mathbf{2}\ H_2S(g) + \mathbf{3}\ O_2(g) \rightarrow SO_2(g) + H_2O(g)$$

The coefficients of the products can easily be obtained by balancing the atoms whose oxidation numbers have changed, and then any other atoms. The final balanced equation is shown below:

$$\mathbf{2}\ H_2S(g) + \mathbf{3}\ O_2(g) \rightarrow \mathbf{2}\ SO_2(g) + \mathbf{2}\ H_2O(g)$$

Sometimes you may not know all of the reactants and products of a redox reaction. The main reactants and oxidized/reduced products will always be given and you will know if the reaction took place in an acidic or basic solution. Experimental evidence shows that water molecules, hydrogen ions, and hydroxide ions play important roles in reactions in such solutions. The procedure for balancing such equations is initially the same as the one used in Sample Problem 13.11, but you will need to add water molecules, hydrogen ions, and/or hydroxide ions to finish the balancing of the overall equation. The following two sample problems illustrate this procedure.

SAMPLE problem 13.12

Chlorate ions and iodine react in an acidic solution to produce chloride ions and iodate ions. Balance the equation for this reaction.

$$ClO_3^-(aq) + I_2(aq) \rightarrow Cl^-(aq) + IO_3^-(aq)$$

Assign oxidation numbers to each atom/ion and note which numbers change.

$$\overset{+5\ -2}{ClO_3^-(aq)} + \overset{0}{I_2(aq)} \rightarrow \overset{-1}{Cl^-(aq)} + \overset{+5\ -2}{IO_3^-(aq)}$$

A chlorine atom is reduced from +5 to −1, a change of 6. Simultaneously, an iodine atom is oxidized from 0 to +5, a change of 5. Record the change in the number of electrons per atom, and per molecule or polyatomic ion.

$$\overset{+5\ -2}{ClO_3^-(aq)} + \overset{0}{I_2(aq)} \rightarrow \overset{-1}{Cl^-(aq)} + \overset{+5\ -2}{IO_3^-(aq)}$$

$6\ e^-/Cl$ $\qquad$ $5\ e^-/I$

$6\ e^-/ClO_3^-$ $\qquad$ $10\ e^-/I_2$

The total number of electrons transferred by each reactant must be the same. Multiply the numbers of electrons by the simplest whole numbers to make the totals equal, in this case, 30 e^-. You can now write the coefficients for the reactants and the products.

$$\overset{+5\ -2}{\mathbf{5}\ ClO_3^-(aq)} + \overset{0}{\mathbf{3}\ I_2(aq)} \rightarrow \overset{-1}{\mathbf{5}\ Cl^-(aq)} + \overset{+5\ -2}{\mathbf{6}\ IO_3^-(aq)}$$

$6\ e^-/Cl$ $\qquad$ $5\ e^-/I$

$6\ e^-/ClO_3^-$ $\qquad$ $10\ e^-/I_2$

$\times\ \mathbf{5}$ $\qquad$ $\times\ \mathbf{3}$

Although the chlorine and iodine atoms are now balanced, notice that the oxygen atoms are not; 15 on the left versus 18 on the right. Because this reaction occurs in an aqueous solution, we can add H_2O molecules to balance the O atoms. The reactant side requires three oxygen atoms (from three water molecules) to equal the total of 18 oxygen atoms on the product side.

$$\mathbf{3\ H_2O(l)} + 5\ ClO_3^-(aq) + 3\ I_2(aq) \rightarrow 5\ Cl^-(aq) + 6\ IO_3^-(aq)$$

In adding water molecules, we are also adding H atoms. Because this reaction occurs in an acidic solution, we will add $H^+(aq)$ to balance the hydrogen.

$$3\ H_2O(l) + 5\ ClO_3^-(aq) + 3\ I_2(aq) \rightarrow 5\ Cl^-(aq) + 6\ IO_3^-(aq) + \mathbf{6\ H^+(aq)}$$

The redox equation should now be completely balanced. Check your work by checking the total numbers of each atom/ion on each side and checking the total electric charge, which should also be balanced.

Learning Tip

A balanced chemical reaction equation includes both a mass and charge balance. Mass is balanced using the atomic symbols. *If the symbols balance, but not the charge, the equation is not balanced.* Be sure to check both the symbols and charges.

DID YOU KNOW

Aboriginal Food Preservation Technology

Pemmican, from the Cree word "pimikan," is a mixture of dried, ground red meat, dried berries, and fat or grease from bone marrow (**Figure 5**). When stored in skin or intestine bags (essentially becoming vacuum-sealed), the pemmican can be kept unspoiled for months or even years. This Aboriginal technology solved a problem that Western scientists recognize today as the oxidation of lipids and proteins by aerobic bacteria, the main culprit in the spoilage of meat.

Figure 5
Pemmican

SAMPLE problem 13.13

Methanol reacts with permanganate ions in a basic solution. The main reactants and products are shown below. Balance the equation for this reaction.

$$CH_3OH(aq) + MnO_4^-(aq) \rightarrow CO_3^{2-}(aq) + MnO_4^{2-}(aq)$$

We will follow the same procedure as in the previous problem, adjusting for a basic solution at the end: assign oxidation numbers; note which ones change and by how much per reactant; and then balance the total number of electrons to obtain the coefficients for the main reactants and products.

$$\overset{-2\,+1\,-2\,+1}{\mathbf{1}\ CH_3OH(aq)} + \overset{+7\,-2}{\mathbf{6}\ MnO_4^-(aq)} \rightarrow \overset{+4\,-2}{\mathbf{1}\ CO_3^{2-}(aq)} + \overset{+6\,-2}{\mathbf{6}\ MnO_4^{2-}(aq)}$$

$6\ e^-/C$	$1\ e^-/Mn$
$6\ e^-/CH_3OH$	$1\ e^-/MnO_4^-$
$\times\ \mathbf{1}$	$\times\ \mathbf{6}$

Just as before, add $H_2O(l)$ to balance the O atoms. The reactant side requires two oxygen atoms (from two water molecules) to equal the 27 oxygen atoms on the product side. Next, balance the H atoms using $H^+(aq)$. The product side requires eight hydrogen ions to balance the eight hydrogen atoms on the reactant side (four in water and four in methanol).

$$\mathbf{2\ H_2O(l)} + CH_3OH(aq) + 6\ MnO_4^-(aq) \rightarrow CO_3^{2-}(aq) + 6\ MnO_4^{2-}(aq) + \mathbf{8\ H^+(aq)}$$

If this reaction occurred in an acidic solution, you would now be finished. For a basic solution, however, we must add enough $OH^-(aq)$ to both sides to equal the number of $H^+(aq)$ present. The hydrogen and hydroxide ions on the same side of the equation are then combined to form water.

$$\mathbf{8\ OH^-(aq)} + 2\ H_2O(l) + CH_3OH(aq) + 6\ MnO_4^-(aq) \rightarrow CO_3^{2-}(aq) + 6\ MnO_4^{2-}(aq) + 8\ H^+(aq) + \mathbf{8\ OH^-(aq)}$$

$$\mathbf{8\ H_2O}$$

Finally, cancel the same number of H_2O molecules on both sides. In this case, the H_2O on the reactant side can be cancelled by also removing $2\ H_2O$ from the product side, leaving the extra $6\ H_2O$ in the final equation.

$$8\ OH^-(aq) + CH_3OH(aq) + 6\ MnO_4^-(aq) \rightarrow CO_3^{2-}(aq) + 6\ MnO_4^{2-}(aq) + 6\ H_2O(l)$$

Learning Tip

Once the main reactants and products are balanced, an alternate procedure is to:

- balance the charge using $OH^-(aq)$
- balance the hydrogen using $H_2O(l)$
- use the oxygen count as a check on your work

COMMUNICATION example 3

Household bleach contains sodium hypochlorite. Some of the hypochlorite ions disproportionate (react with themselves) to produce chloride ions and chlorate ions. Write the balanced redox equation for the disproportionation.

Solution

$$\overset{+1\,-2}{2\ ClO^-(aq)} + \overset{+1\,-2}{ClO^-(aq)} \rightarrow \overset{-1}{2\ Cl^-(aq)} + \overset{+5\,-2}{ClO_3^-(aq)}$$

$2\ e^-/Cl$	$4\ e^-/Cl$
$2\ e^-/ClO^-$	$4\ e^-/ClO^-$
$\times\ 2$	$\times\ 1$

$$3\ ClO^-(aq) \rightarrow 2\ Cl^-(aq) + ClO_3^-(aq)$$

Learning Tip

For disproportionation reactions, start with two identical entities on the reactant side and follow the usual procedure for balancing equations.

COMMUNICATION example 4

Balance the chemical equation for the oxidation of ethanol by dichromate ions in a breathalyzer (**Figure 6**) to form chromium(III) ions and acetic acid in an acidic solution.

Solution

$$\overset{+6\ -2}{16\ H^+(aq) + 2\ Cr_2O_7^{2-}(aq)} + \overset{-2+1\ \ -2\ +1}{3\ C_2H_5OH(aq)} \rightarrow \overset{+3}{4\ Cr^{3+}(aq)} + \overset{0\ +1\ 0\ -2-2\ +1}{3\ CH_3COOH(aq)} + 11\ H_2O(l)$$

$3\ e^-/Cr$ $\qquad$ $2\ e^-/C$

$6\ e^-/Cr_2O_7^{2-}$ $\qquad$ $4\ e^-/C_2H_5OH$

$\times 2$ $\qquad$ $\times 3$

Learning Tip

Compare the solution in Communication Example 4 with the solution in Sample Problem 13.6 (page 580). These represent different approaches to the same question. In this section, you should practise the oxidation number method. On tests, you will usually choose your method.

SUMMARY Balancing Redox Equations Using Oxidation Numbers

Step 1: Assign oxidation numbers and identify the atoms/ions whose oxidation numbers change.

Step 2: Using the change in oxidation numbers, write the number of electrons transferred per atom.

Step 3: Using the chemical formulas, determine the number of electrons transferred per reactant. (Use the formula subscripts to do this.)

Step 4: Calculate the simplest whole number coefficients for the reactants that will balance the total number of electrons transferred. Balance the reactants and products.

Step 5: Balance the O atoms using $H_2O(l)$, and then balance the H atoms using $H^+(aq)$.

For basic solutions only

Step 6: Add $OH^-(aq)$ to both sides equal in number to the number of $H^+(aq)$ present.

Step 7: Combine $H^+(aq)$ and $OH^-(aq)$ on the same side to form $H_2O(l)$, and cancel the same number of $H_2O(l)$ on both sides.

Figure 6
The original breath alcohol testing device uses the reaction of ethanol with acidic dichromate solution. More modern devices, like the one shown, use the reaction of ethanol in a fuel cell to determine the blood alcohol count.

Practice

11. Why is the change in oxidation number of an atom the same as the number of electrons transferred?

12. Balance the following chemical equations for reactions in an acidic solution:
(a) $Cr_2O_7^{2-}(aq) + Cl^-(aq) \rightarrow Cr^{3+}(aq) + Cl_2(aq)$
(b) $IO_3^-(aq) + HSO_3^-(aq) \rightarrow SO_4^{2-}(aq) + I_2(s)$
(c) $HBr(aq) + H_2SO_4(aq) \rightarrow SO_2(g) + Br_2(l)$

13. Balance the following chemical equations for reactions in a basic solution:
(a) $MnO_4^-(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + MnO_2(s)$
(b) $ClO_3^-(aq) + N_2H_4(aq) \rightarrow NO(g) + Cl^-(aq)$

14. For the reactions in question 13, identify the oxidizing agents and the reducing agents.

15. Ammonia gas undergoes a combustion to produce nitrogen dioxide gas and water vapour. Write and balance the reaction equation.

Case Study

Bleaching Wood Pulp

The production of pulp and paper is one of Canada's major industries (**Figure 7**), employing several thousand people across the country and contributing billions of dollars to Canada's export market. The processes used in the pulp and paper industry illustrate how a successful technology can have both intended and unintended consequences.

Modern chemistry and chemical technology make it possible for cellulose fibres from wood pulp to be bleached, dyed, coated, and treated to manufacture paper, as well as cellophane and explosives. The production of white paper involves a bleaching process in which a strong oxidizing agent oxidizes coloured organic compounds. For many years, the oxidizing agent was elemental chlorine, which breaks down and removes lignin, an organic polymer that binds the wood fibres together. Over 300 reaction by-products, including chloroform, carbon tetrachloride, chlorophenols, and furans, are produced during the process.

Many of these by-products are potentially harmful. Research indicates that, although only one of 75 dioxin isomers is extremely toxic, some dioxins can cause immune system suppression and severe reproductive disorders, including birth defects and sterility. Also, certain dioxins are potent carcinogens. Once in the ecosystem, dioxins resist breakdown and bioaccumulate in animal tissues. Traces of dioxins have been found in bleached paper products such as diapers, sanitary products, paper plates, toilet paper, coffee filters, food packaging, and writing paper.

In the 1980s, growing concern over toxic chemicals entering the ecosystem from pulp mill effluent prompted the Canadian government to implement stricter environmental regulations. As a result, the pulp and paper industry underwent the largest environmental upgrade in its history. The use of elemental chlorine for bleaching was reduced or replaced, which produced a corresponding reduction in the emission of dioxins and furans. In addition, the recycling of paper increased and the water consumption per tonne of paper decreased. Overall, the effluent quality has vastly improved, although its adverse effects on fish and other aquatic organisms are still being seen.

Industry researchers proposed multiple solutions, many of which were implemented to reduce the quantities of toxic chemicals produced by pulp mills. Each solution involved different designs, materials, and processes. Some of the measures introduced to reduce the emission of organochlorines include: more efficient washing of pulp; oxygen pre-bleaching; using chlorine dioxide, hydrogen peroxide, or ozone instead of elemental chlorine; and bleaching to a lesser degree. While these new technologies are reducing the negative impact of pulp mills on the environment, there is concern that they, too, will have some unintended effects on the environment.

Figure 7
There are over 150 pulp and paper mills in Canada. Canada is the fourth largest producer in the world of pulp and paper products, and the world's largest supplier of newsprint.

Case Study Questions

1. What were the unintended consequences of using chlorine to bleach wood pulp?
2. List some new processes that were developed to reduce the problems created by bleaching wood pulp with chlorine.
3. Describe the perspectives that need to be considered when selecting the chemical to replace elemental chlorine in the bleaching process.
4. The most common alternative to the use of elemental chlorine as a bleaching agent is chlorine dioxide gas. In addition to having a less negative environmental impact, chlorine dioxide has a greater oxidizing ability. Assuming both chlorine and chlorine dioxide are converted to chloride ions, use oxidation numbers to show the greater oxidizing ability of chlorine dioxide.

Extension

5. Investigate at least two pulp and paper companies (one in Canada and one outside of North America) to see what actions they have taken to reduce their impact on the environment. Present your findings in a medium of your choice.

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6. Research several reactions involved in the bleaching of paper, and balance or verify the balancing of the reaction equations using oxidation numbers.

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Section 13.3 Questions

1. Copy and complete the following table to distinguish between oxidation and reduction:

	Electron transfer	Oxidation states
oxidation		
reduction		

2. Define an oxidation number.

3. State two ways in which you can recognize a redox reaction, using a chemical reaction equation.

4. Write the oxidation number of each atom/ion in the following substances:
(a) carbon monoxide, CO(g), a toxic gas
(b) ozone, $O_3(g)$, ozone layer
(c) ammonium chloride, $NH_4Cl(s)$, used in dry cells (batteries)
(d) phosphoric acid, $H_3PO_4(aq)$, in cola soft drinks
(e) sodium thiosulfate, $Na_2S_2O_3(s)$, antidote for cyanide poisoning
(f) sodium tripolyphosphate, $Na_5P_3O_{10}(s)$, in laundry detergents

5. Assigning oxidation numbers using the rules we have established may occasionally produce some unusual results. For example, consider Fe_3O_4.
(a) Determine the oxidation number of iron in Fe_3O_4.
(b) What is unusual about your answer? Suggest a reason for your answer.

6. Redox reactions are common in organic chemistry. For example, carboxyl groups can be oxidized to form carbon dioxide. In the following chemical equation, permanganate ions convert oxalate ions to carbon dioxide in an acidic solution.

$$2\,MnO_4^-(aq) + 5\,C_2O_4^{2-}(aq) + 16\,H^+(aq) \rightarrow 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 10\,CO_2(g)$$

(a) Assign oxidation numbers to all atoms/ions.
(b) Which atom is oxidized? State the change.
(c) Which atom is reduced? State the change.
(d) Identify the oxidizing and reducing agents.

7. When carbon dioxide is released into the atmosphere from natural or human activities, some of it reacts with water to form carbonic acid. This accounts for the natural acidity of rainwater and may also contribute to acid rain.
(a) Write the balanced chemical equation for the reaction of carbon dioxide with water to form carbonic acid.
(b) Is this a redox reaction? Justify your answer.

8. Balance the following equations representing reactions that occur in an acidic solution:
(a) $Cu(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$
(b) $H_2O_2(aq) + Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq) + O_2(g) + H_2O(l)$
(c) $Mn^{2+}(aq) + HBiO_3(aq) \rightarrow Bi^{3+}(aq) + MnO_4^-(aq)$

9. Balance the following equations representing a reaction that occurs in a basic solution:
(a) $Cr(OH)_3(s) + IO_3^-(aq) \rightarrow CrO_4^{2-}(aq) + I^-(aq)$
(b) $Ag_2O(s) + HCHO(aq) \rightarrow Ag(s) + HCO_2^-(aq)$
(c) $S_2O_4^{2-}(aq) + O_2(g) \rightarrow SO_4^{2-}(aq)$

10. Hydrogen peroxide decomposes in the presence of a catalyst to form water and oxygen gas. Use oxidation numbers to show that this reaction is a disproportionation.

11. State two general experimental designs that could help determine the balancing of the main species in a redox reaction.

12. Evidence shows that iron(III) sulfide reacts according to the following balanced redox equation:

$$2\,Fe_2S_3(s) + 6\,H_2O(l) + 11\,O_2(g) \rightarrow 4\,FeO(s) + 6\,H_2SO_4(aq)$$

(a) List the oxidation numbers for all entities in this reaction equation.
(b) Identify the entities that are oxidized and reduced.
(c) How does this reaction equation illustrate the limitations of the method presented to balance redox reaction equations?

Extension

13. How is the making of pemmican by First Nations peoples an example of technology providing solutions to practical problems? List some advantages of pemmican and state its importance to early European explorers and settlers.

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14. Most organisms derive their metabolic energy from cellular respiration, making this one of the most important biological redox processes. Outline the chemistry of cellular respiration. Your response should include:
- the overall chemical reaction equation for cellular respiration, with the oxidation, reduction, oxidizing agent, reducing agent, and overall direction of electron transfer indicated
- brief descriptions of the three main stages of aerobic respiration

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15. Science terms and concepts are often used to help promote a variety of new technologies marketed to consumers. One recent example is the titanium necklace or bracelet. Refer to Appendix B.4 and use the Internet to answer the following questions.
(a) List some science terms and concepts that are mentioned in the promotion of this product.
(b) Briefly summarize the claims implied by the manufacturer.
(c) What kind of evidence is presented to justify the claims?
(d) Write a brief experimental design to conduct a scientific test of the claims and collect more reliable evidence.

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13.4 Redox Stoichiometry

The stoichiometric method can be used to predict or analyze the quantity of a chemical involved in a chemical reaction. You encountered many applications of stoichiometry in Chapter 7 involving masses, volumes, and concentrations of reactants and products. For the stoichiometry calculations in Chapter 7, you assumed that all the reactions were spontaneous, fast, stoichiometric, and quantitative. These same assumptions apply to redox stoichiometry.

There are many industrial and laboratory applications of redox stoichiometry. For example, a mining engineer must know the concentration of iron in a sample of iron ore in order to decide whether or not a mine would be profitable. Chemical technicians in industry, monitoring the quality of their companies' products, must determine the concentration of substances such as sodium hypochlorite (NaClO) in bleach, or hydrogen peroxide (H_2O_2) in disinfectants. Hospital laboratory technicians and environmental chemists detect tiny traces of chemicals by a variety of methods. Although much analytical chemistry involves sophisticated equipment, the basic technological process of titration still has an important role (Appendix C.4).

Figure 1
Titration is a common experimental design for quantitative chemical analysis.

In a titration, one reagent (the *titrant*) is slowly added to another (the *sample*) until an abrupt change in a solution property (the *endpoint*) occurs (**Figure 1**). In acid–base titrations, the titrant is generally a strong acid or base. In redox titrations, the titrant is always a strong oxidizing or reducing agent. Two oxidizing agents commonly used in redox titrations are acidic solutions of permanganate ions or dichromate ions. They are both strong oxidizing agents and undergo a colour change when they oxidize a reducing agent in a sample being titrated. The permanganate ion, which has an intense purple-pink colour in solution, changes to the essentially colourless manganese(II) ion in a reaction with a reducing agent that is usually colourless (**Figure 2**).

Figure 2
A solution of potassium permanganate is being added to an acidic solution of iron(II) ions. The dark purple-pink colour of $MnO_4^-(aq)$ ions instantly disappears as they react with iron(II) ions to produce the almost colourless $Mn^{2+}(aq)$.

$$\underset{\text{purple-pink}}{MnO_4^-(aq)} + 8\,H^+(aq) + 5\,e^- \rightarrow \underset{\text{colourless}}{Mn^{2+}(aq)} + 4\,H_2O(l)$$

Once the reducing agent in the sample has completely reacted, the next drop of permanganate added remains unreacted and causes a pink colour in the mixture. The colour change of the reaction mixture (colourless to pink) is the endpoint and corresponds to a slight excess of unreacted permanganate ion. The volume of permanganate solution added when the endpoint is reached is a measurement of the point at which stoichiometric quantities of reactants have been combined.

The dichromate ion is also commonly used in redox titrations; however, its colour change is not as easy to see: the orange dichromate solution gradually changes to a green chromium(III) solution. A redox indicator is usually added to produce a sharper endpoint.

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + 14\,H^+(aq) + 6\,e^- \rightarrow \underset{\text{green}}{2\,Cr^{3+}(aq)} + 7\,H_2O(l)$$

When a titration is used to analyze the concentration of a sample, the concentration of the titrant used must be accurately known. If the titrant is not a standard solution, the titrant is standardized by calculating its concentration using evidence from an analysis with a primary standard. A *primary standard* is a chemical that can be used directly to prepare a standard solution—a solution of precisely known concentration (refer to Unit 4).

SAMPLE problem 13.14

A solution of potassium permanganate cannot be directly prepared with a precisely known concentration because the permanganate ion reacts with organic and inorganic impurities in the water and with the water itself. Thus, potassium permanganate is not used as a primary standard. Complete the Analysis of the investigation report.

Problem

What is the concentration of the potassium permanganate solution?

Design

A freshly prepared solution of potassium permanganate is titrated against samples of acidic tin(II) chloride solution, which has a known concentration. The tin(II) chloride solution is the primary standard.

Evidence

Table 1 Titration of 10.00 mL of Acidic 0.0500 mol/L $SnCl_2(aq)$ with $KMnO_4(aq)$

Trial	1	2	3	4
final burette reading (mL)	18.4	35.3	17.3	34.1
initial burette reading (mL)	1.0	18.4	0.6	17.3
volume of $KMnO_4(aq)$ (mL)	17.4	16.9	16.7	16.8
endpoint colour	dark pink	light pink	light pink	light pink

Analysis

The Analysis for a titration experiment follows the same general stoichiometry steps that you practiced in Unit 4. The main difference is that you have a much more sophisticated way of writing the chemical reaction equation.

The first endpoint was overshot and was not used in the average for the analysis. At the endpoint, an average of 16.8 mL of permanganate solution was used.

OA SOA OA OA OA

$K^+(aq)$ $MnO_4^-(aq)$ $H^+(aq)$ $Sn^{2+}(aq)$ $Cl^-(aq)$ $H_2O(l)$

SRA RA RA RA

$$2\,[MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

$$5\,[Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,e^-]$$

$$2\,MnO_4^-(aq) + 16\,H^+(aq) + 5\,Sn^{2+}(aq) \rightarrow 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 5\,Sn^{4+}(aq)$$

16.8 mL	10.00 mL
c	0.0500 mol/L

$$n_{Sn^{2+}} = 10.00\text{ mL} \times \frac{0.0500\text{ mol}}{1\text{ L}} = 0.500\text{ mmol}$$

$$n_{MnO_4^-} = 0.500\text{ mmol} \times \frac{2}{5} = 0.200\text{ mmol}$$

$$[MnO_4^-] = \frac{0.200\text{ mmol}}{16.8\text{ mL}} = 0.0119\text{ mol/L or } 11.9\text{ mmol/L}$$

$$\text{or } [MnO_4^-] = 10.00\,\cancel{\text{mL Sn}^{2+}} \times \frac{0.0500\,\cancel{\text{mol Sn}^{2+}}}{1\,\cancel{\text{L Sn}^{2+}}} \times \frac{2\text{ mol } MnO_4^-}{5\,\cancel{\text{mol Sn}^{2+}}} \times \frac{1}{16.8\,\cancel{\text{mL}}\,MnO_4^-}$$

$$= 0.0119\text{ mol/L}$$

According to the evidence gathered and the stoichiometric analysis, the amount concentration of the potassium permanganate solution is 0.0119 mol/L or 11.9 mmol/L.

DID YOU KNOW?

Scientific Credibility

For credibility, scientific claims must be testable empirically. The results of any tests must be replicated by further experimentation. The same person might repeat the measurements, in a titration, for example, or members of the same research team might repeat the experiment. The scientific community accepts new scientific discoveries only if different scientists in different laboratories are able to reproduce the results.

Learning Tip

The general stoichiometry procedure is as follows:

1. Write a balanced chemical equation with measurements and conversion factors.
2. Convert given measurements into a chemical amount.
3. Calculate the amount of the required substance using the mole ratio.
4. Convert this calculated amount to the final requested quantity.

DID YOU KNOW?

Standardized Solution

The *standardized* potassium permanganate solution can be used as a strong oxidizing agent in further titrations. A laboratory technician might standardize the solution in the morning, and then re-standardize at noon and at the end of the day to increase the certainty of the results.

LAB EXERCISE 13.C

Analyzing for Tin

Extensive long-term research has found that treating children's teeth with fluoride significantly reduces tooth decay. When this was first discovered, toothpastes were produced containing tin(II) fluoride. Complete the Analysis of the investigation report.

Purpose

The purpose of this lab exercise is to use the stoichiometric method in a redox chemical analysis.

Problem

What is the amount concentration of tin(II) ions in a solution prepared for research on toothpaste?

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ○ Evidence
- ● Analysis
- ○ Evaluation

Evidence

Table 2 Titration of 10.00 mL of acidic $Sn^{2+}(aq)$ with 0.0832 mol/L $KMnO_4(aq)$

Trial	1	2	3
final burette reading (mL)	15.8	28.1	40.6
initial burette reading (mL)	3.4	15.8	28.1
volume of $KMnO_4(aq)$ (mL)	12.4	12.3	12.5

Figure 3
Imants Lauks (1952–)

WWW WEB Activity

Canadian Achievers—Imants Lauks

Dr. Imants Lauks (**Figure 3**) is a world leader in developing biochips for clinical diagnostic products. He invented the silicon chip blood analyzer in 1986. Biochips combine silicon chip technology with chemical reactions, many of which are electrochemical (redox) reactions.

1. Describe the FlexCard™ technology that Dr. Lauks' current company, Epocal, is developing.
2. What practical problems does this technology solve?

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Practice

1. Titration is a common experimental procedure for the quantitative analysis of chemical substances. What are the four requirements for titration experiments?
2. Titration is one of several experimental procedures that can be used to determine the quantity of a chemical in a sample. What are some alternative designs available for this purpose?
3. Silver metal can be recycled by reacting nickel metal with waste silver ion solutions. What volume of 0.10 mol/L silver ion solution will react completely with 25.0 g of nickel metal?
4. In a chemical analysis of a chromium alloy, all of the chromium is first converted to chromate ions. A 50.0 mL sample of the chromate ion solution is then reduced in a basic solution to chromium(III) hydroxide by reaction with 22.6 mL of 1.08 mol/L sodium sulfite. In this reaction, the sulfite ions are oxidized to sulfate ions. What is the amount concentration of the chromate ion solution?
5. Pure iron metal may be used as a primary standard for permanganate solutions. A 1.08 g sample of pure iron wire was dissolved in acid, converted to iron(II) ions, and diluted to 250.0 mL. In the titration, an average volume of 13.6 mL of permanganate solution was required to react with 10.0 mL of the acidic iron(II) solution. Calculate the amount concentration of the permanganate solution.

LAB EXERCISE 13.D

Analyzing for Chromium in Steel

Stainless steel is a corrosion-resistant, esthetically pleasing alloy, normally composed of nickel, chromium, and iron. Complete the Analysis of the investigation report.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	○ Evaluation
○ Hypothesis	○ Procedure	
○ Prediction	○ Evidence	

Purpose

The purpose of this lab exercise is to use the stoichiometric method in a redox chemical analysis.

Problem

What is the amount concentration of chromium(II) ions in a solution obtained in the analysis of a stainless steel alloy?

Design

A standard potassium dichromate solution is used as an oxidizing agent to oxidize chromium(II) ions to chromium(III) ions in an acidic solution (**Figure 4**).

Evidence

Table 3 Titration of 10.00 mL of acidic $Cr^{2+}(aq)$ with 0.125 mol/L $K_2Cr_2O_7(aq)$

Trial	1	2	3
final burette reading (mL)	17.5	34.9	18.9
initial burette reading (mL)	0.1	17.5	1.5
volume of $K_2Cr_2O_7(aq)$ (mL)	17.4	17.4	17.4

Figure 4
The blue $Cr^{2+}(aq)$ solution is oxidized to a green $Cr^{3+}(aq)$ solution.

INVESTIGATION 13.4 *Introduction*

Analyzing a Hydrogen Peroxide Solution

In this investigation, you assume the role of a laboratory technician working in a consumer advocacy laboratory, testing the concentration of a hydrogen peroxide solution. The labelled percent concentration of hydrogen peroxide on the commercial product is used for the Prediction.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	● Materials	● Evaluation (1, 2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Purpose

The technological purpose of this investigation is to test and evaluate the percent concentration of the consumer solution of hydrogen peroxide.

Problem

What is the percent concentration of hydrogen peroxide in a consumer product?

Design

An acidic solution of the primary standard, iron(II) ammonium sulfate–water (1/6), is prepared and the potassium permanganate solution is standardized by a titration with this primary standard. A 25.0 mL sample of a consumer solution of hydrogen peroxide is diluted to 1.00 L with water (that is, it is diluted by a factor of 40). The standardized potassium permanganate solution is used to titrate the diluted and acidified hydrogen peroxide. The amount concentration of the original hydrogen peroxide is obtained by analysis of the titration evidence, and by using a graph, prepared with a graphing calculator or computer spreadsheet program, of the amount and percent concentration of aqueous hydrogen peroxide.

To perform this investigation, turn to page 603.

Section 13.4 Questions

1. State the similarities and differences between the method for redox stoichiometry and other examples of stoichiometry.
2. In acid–base titrations, one reactant (usually the titrant) is a strong acid or strong base. Similarly, in a redox stoichiometry, the reactant used to analyze a sample of unknown concentration is either a strong oxidizing or strong reducing agent.
   (a) State two common strong oxidizing agents commonly used in a redox titration.
   (b) Using the redox table, suggest a strong reducing agent that might be suitable for a redox titration analysis.
   (c) What are some examples of other strong reducing agents that might be used in an analysis? What type of experimental design would be appropriate?
3. Why is it necessary to standardize a potassium permanganate solution to be used in a chemical analysis?
4. In a chemical analysis, 10.00 mL samples of aqueous hydrogen peroxide are acidified and then titrated with 0.200 mol/L sodium perchlorate solution. From the evidence, an average volume of 24.0 mL of aqueous sodium perchlorate is required to reach the endpoint. Calculate the amount concentration of the hydrogen peroxide solution.
5. Complete the Analysis and Evaluation (of the prediction and, thus, of the metallurgical process) of the investigation report.

   Purpose
   The purpose of this lab exercise is to use redox stoichiometry to evaluate a technological process.

   Problem
   What is the amount concentration of iron(II) ions in a solution obtained in an iron ore analysis?

   Prediction
   According to the required standards for the metallurgical process, the concentration of the iron(II) ions should be 80.0 mmol/L.

   Design
   The iron(II) solution is titrated to iron(III) with a standard cerium(IV) ion solution, which is reduced to cerium(III). The indicator shows, as the endpoint, a sharp colour change from red to pale blue.

   Evidence

   Table 4 Titration of 25.0 mL of $Fe^{2+}(aq)$ with 0.125 mol/L $Ce^{4+}(aq)$

Trial	1	2	3	4
final burette reading (mL)	15.7	30.7	45.6	40.2
initial burette reading (mL)	0.6	15.7	30.7	25.3

6. A scientist used the titration method to analyze for tin(II) chloride. Complete the two steps of the Analysis.

   Problem
   What is the amount concentration of a tin(II) chloride solution prepared from a sample of tin ore?

   Design
   The potassium dichromate solution is first standardized by titration with 10.00 mL of an acidified 0.0500 mol/L solution of the primary standard, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O(s)$. The standardized dichromate solution is then titrated against 10.00 mL of the acidified tin(II) chloride solution.

   Evidence

   Table 5 Titration of 10.00 mL of 0.0500 mol/L $Fe^{2+}(aq)$ with $K_2Cr_2O_7(aq)$

Trial	1	2	3	4
final burette reading (mL)	13.8	24.4	35.2	45.9
initial burette reading (mL)	2.3	13.8	24.4	35.2

   Table 6 Titration of 10.00 mL of $Sn^{2+}(aq)$ with $K_2Cr_2O_7(aq)$

Trial	1	2	3	4
final burette reading (mL)	11.8	22.9	33.9	45.0
initial burette reading (mL)	0.3	11.8	22.9	33.9

Extension

7. Potassium dichromate is a common reagent used in the analysis of the iron content of iron ore samples. If each analysis begins with the same mass of the ore, a redox titration can be designed such that the volume of dichromate required corresponds to the percent iron in the ore. This design eliminates the need for any calculations, so rapid, efficient analyses can be carried out by technicians. Starting with a 1.00 g sample of iron ore, the sample is treated to convert all the iron into iron(II) ions, and then acidified. Predict the concentration of potassium dichromate required so that the volume (in millilitres) equals the percentage of iron in the original sample.

INVESTIGATION 13.1

Single Replacement Reactions

This investigation is a review of single replacement reactions in preparation for the development of a theory of oxidation and reduction. As part of the Design, include diagnostic tests (as in Appendix C.4) for the predicted products.

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	○ Materials	● Evaluation (1)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Purpose

The purpose of this investigation is to use the single replacement reaction generalization to predict and analyze the reactants and products.

Problem

What are the products of the single replacement reactions for the following pairs of reactants?

(a) copper and aqueous silver nitrate

(b) aqueous chlorine and aqueous sodium bromide

(c) magnesium and hydrochloric acid

(d) zinc and aqueous copper(II) sulfate

(e) aqueous chlorine and aqueous potassium iodide

Materials

lab apron
eye protection
five small test tubes
two test tube stoppers
test tube rack
steel wool
wash bottle
matches
copper strip
chlorine water
magnesium ribbon
zinc strip
aqueous silver nitrate
aqueous sodium bromide
hydrochloric acid
aqueous copper(II) sulfate
aqueous potassium iodide
hexane

Toxic, corrosive, and irritant chemicals are used in this investigation. Avoid skin contact. Wash any splashes on the skin or clothing with plenty of water. If any chemical is splashed in the eye, rinse for at least 15 min and inform your teacher.

Keep the hexane sealed to avoid evaporation. Dispose of the hexane as directed by your teacher. Hexane is highly flammable. Keep away from open flame. Make sure matches are extinguished by dipping in water. Do not inhale the vapours.

Procedure

1. Set up five test tubes, each filled to a depth of 2–3 cm with one of the five aqueous solutions.
2. Add the element indicated to each test tube.
3. Perform diagnostic tests on each of the five mixtures. Record your evidence.
4. Dispose of the solutions as directed by your teacher.

INVESTIGATION 13.2

Spontaneity of Redox Reactions

In previous units in this textbook, we assumed that all chemical reactions are spontaneous; that is, they occur once the reactants are placed in contact, without a continuous addition of energy to the system. Spontaneous redox reactions in solution generally provide visible evidence of a reaction within a few minutes.

Purpose
The purpose of this investigation is to test the assumption that all single replacement reactions are spontaneous.

Problem
Which combinations of copper, lead, silver, and zinc metals and their aqueous metal ion solutions produce spontaneous reactions?

Design
A drop of each solution is placed in separate locations on a clean area of each of the four metal strips.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (1, 2, 3)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

Materials
lab apron
eye protection
reusable strips of copper, lead, silver, and zinc metals
(*Note that the lead strips bend much more easily than the zinc strips, which look similar.*)
0.10 mol/L solutions of copper(II) nitrate, lead(II) nitrate, silver nitrate, and zinc nitrate in dropper bottles
steel wool or sandpaper

These chemicals are toxic—especially the lead solution—and irritants. Avoid skin contact. Remember to wash your hands before leaving the laboratory. Rinse all of the metal strips thoroughly and return them so they can be used again.

INVESTIGATION 13.3

Predicting the Reaction of Sodium Metal (Demonstration)

The process of developing theories, laws, and generalizations requires that they must be tested numerous times in as many different situations as possible. This process is necessary not only to determine their validity, but also to identify exceptions that may lead to new knowledge.

As part of the Design, include a list of diagnostic tests using the "If [procedure] and [evidence], then [analysis]" format for every product predicted. (This format is described in Appendix C.4.)

Purpose
The purpose of this demonstration is to test the five-step method for predicting redox reactions.

Problem
What are the products of the reaction of sodium metal with water?

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	○ Materials	● Evaluation (1, 2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

This reaction of sodium metal must be demonstrated with great care, because a great deal of heat is produced. Use only a piece the size of a small pea, use a safety screen, wear a lab apron, eye protection, and face shield, and keep observers at least two metres away.

INVESTIGATION 13.4

Analyzing a Hydrogen Peroxide Solution

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	● Materials	● Evaluation (1, 2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

In this investigation, you assume the role of a laboratory technician working in a consumer advocacy laboratory, testing the concentration of a hydrogen peroxide solution. The labelled percent concentration of hydrogen peroxide on the commercial product is used for the Prediction (**Figure 1**).

Purpose

The technological purpose of this investigation is to test and evaluate the percent concentration of the consumer solution of hydrogen peroxide.

Problem

What is the percent concentration of hydrogen peroxide in a consumer product?

Design

An acidic solution of the primary standard, iron(II) ammonium sulfate–water (1/6), is prepared and the potassium permanganate solution is standardized by a titration with this primary standard. A 25.0 mL sample of a consumer solution of hydrogen peroxide is diluted to 1.00 L with water (that is, it is diluted by a factor of 40). The standardized potassium permanganate solution is used to titrate the diluted and acidified hydrogen peroxide. The amount concentration of the original hydrogen peroxide is obtained by analysis of the titration evidence, and by using a graph, prepared with a graphing calculator or computer spreadsheet program, of the information in **Table 1**.

Materials

lab apron
eye protection
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O(s)$
2 mol/L $H_2SO_4(aq)$
diluted $H_2O_2(aq)$
$KMnO_4(aq)$
(list to be completed by student)

Sulfuric acid is corrosive. Iron(II) ammonium sulfate, hydrogen peroxide, and potassium permanganate are irritants. Avoid inhaling any solid, and avoid skin or eye contact.

Procedure

1. (Pre-lab) Calculate the required mass of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O(s)$ to prepare 100.0 mL of a 0.0500 mol/L solution.

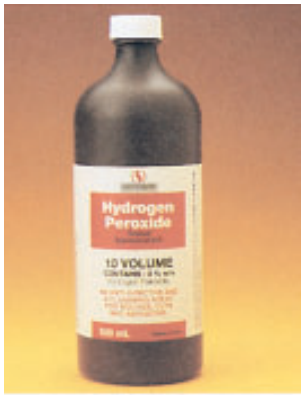

Figure 1
In drugstores, hydrogen peroxide is usually sold as a 3% solution. Hairdressers use a 6% solution.

Table 1 $H_2O_2(aq)$ Concentration

Amount concentration (mol/L)	Percent concentration (%)
0.73	2.5
0.76	2.6
0.79	2.7
0.82	2.8
0.85	2.9
0.88	3.0
0.91	3.1
0.94	3.2
0.97	3.3
1.0	3.4

2. Measure the required mass of the iron(II) compound in a clean, dry 100 mL beaker.
3. Dissolve the solid in about 40 mL of $H_2SO_4(aq)$.
4. Transfer this solution into a clean 100 mL volumetric flask, rinsing and adding pure water to complete the preparation of the standard solution.
5. Transfer 10.00 mL of the standard iron(II) solution by pipette into a clean 250 mL Erlenmeyer flask.
6. Titrate the acidic iron(II) sample with $KMnO_4(aq)$.
7. Repeat steps 5 and 6 until three consistent volumes (within 0.1 mL) are obtained.
8. Transfer 10.00 mL of the diluted hydrogen peroxide solution by pipette into a clean 250 mL Erlenmeyer flask.
9. Using a 10 mL graduated cylinder, add 5 mL of $H_2SO_4(aq)$ to the hydrogen peroxide solution.
10. Titrate the acidic hydrogen peroxide solution with $KMnO_4(aq)$.
11. Repeat steps 8 to 10 until three consistent volumes (within 0.1 mL) are obtained.
12. Dispose of all solutions into a labelled waste container.

Chapter 13 SUMMARY

Outcomes

Knowledge

- define oxidation and reduction operationally (historically) and theoretically (13.1, 13.2, 13.3)
- define the following terms: oxidizing agent, reducing agent, oxidation number, half-reaction, disproportionation (13.1, 13.2, 13.3)
- differentiate between redox reactions and other reactions by identifying half-reactions and changes in oxidation number (13.1, 13.2, 13.3)
- identify electron transfer, oxidizing agents, and reducing agents in redox reactions that occur in everyday life in both living and nonliving systems (all sections)
- compare the relative strengths of oxidizing and reducing agents from empirical data (13.2)
- predict the spontaneity of a redox reaction based on a redox table, and compare predictions to experimental results (13.2)
- write and balance equations for redox reactions in acidic, basic, and neutral solutions, including disproportionation reactions, by using half-reaction equations, developing simple half-reaction equations, and assigning oxidation numbers (13.2, 13.3, 13.4)
- perform calculations to determine quantities of substances involved in redox titrations (13.4)

STS

- state that a goal of technology is to solve practical problems (all sections)
- recognize that technological problems may require various solutions and have both intended and unintended consequences (13.1, 13.2, 13.3)

Skills

- initiating and planning: design an experiment to determine the reactivity of various metals (13.1, 13.2); and describe procedures for safe handling, storing, and disposal of materials used in the laboratory, with reference to WHMIS and consumer product labelling information (13.1, 13.2, 13.4)
- performing and recording: select and use appropriate equipment to perform a redox titration (13.4); use a standard redox table to predict the spontaneity of redox reactions (13.2, 13.4); and create charts, tables, or spreadsheets related to redox reactions (13.1, 13.2, 13.4)
- analyzing and interpreting: analyze evidence from an experiment to derive a simple redox table (13.2); interpret patterns and trends in redox reactions (all sections); and evaluate redox experiments, including identifying the limitations of the evidence (13.1, 13.2, 13.4)
- communication and teamwork: work collaboratively in addressing problems, and select and use appropriate modes of representation for redox reactions and answers to redox problems (all sections)

Key Terms

13.1

half-reaction
reduction
oxidation
redox reaction

13.2

reducing agent
oxidizing agent
redox spontaneity rule
disproportionation

13.3

oxidation number
oxidation
reduction

MAKE a summary

1. Start with "redox" and make a flow chart or concept map that includes all of the Key Terms listed, plus any important generalizations and procedures that will help you learn the material in this chapter.
2. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?

Go To www.science.nelson.com

The following components are available on the Nelson Web site. Follow the links for *Nelson Chemistry Alberta 20–30*.

- an interactive Self Quiz for Chapter 13
- additional Diploma Exam-style Review questions
- Illustrated Glossary
- additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

EXTENSION

CBC radio ONE QUIRKS & QUARKS

Electric Universe

Electricity is everywhere. Only two centuries ago, people developed technologies to release and control electricity. Since then we have come to rely on it for almost every aspect of our lives. A science writer talks about some of the characters who helped to bring electricity into our lives.

www.science.nelson.com GO

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

www.science.nelson.com GO

DO NOT WRITE IN THIS TEXTBOOK.

Part 1

1. Historically, __*i*__ meant producing __*ii*__ from their naturally occurring compounds. According to modern theory, this process involves a __*iii*__ of electrons.

The above statement is completed by the information in which row?

Row	*i*	*ii*	*iii*
A.	oxidation	metals	gain
B.	reduction	metals	gain
C.	oxidation	nonmetals	loss
D.	reduction	nonmetals	loss

2. A reducing agent can be described as a substance that
A. loses electrons and causes reduction
B. loses electrons and becomes reduced
C. gains electrons and causes oxidation
D. gains electrons and becomes reduced

3. Which one of the following general reaction types will *not* be a redox reaction?
A. combustion
B. simple decomposition
C. disproportionation
D. double replacement

4. NR Some natural and technological processes that involve redox reactions are
1. corrosion
2. metallurgy
3. cellular respiration
4. photosynthesis
5. rusting of iron
6. magnesium metal flares

The processes in which oxygen behaves as an oxidizing agent are, **in numerical order**,

___, ___, ___, and ___.

5. Which of the following combinations would produce a spontaneous redox reaction?
A. nitric acid and iron(III) chloride solution
B. chromium metal and aqueous cobalt(II) chloride
C. oxygen gas bubbled into a sodium bromide solution
D. aqueous tin(II) nitrate and potassium iodide solutions

Use this information to answer questions 6 and 7.

Four different metals and their corresponding metal ion solutions are mixed to determine if a spontaneous reaction occurs.

Table 1 Metal–Ion Reactions

	$X^{2+}(aq)$	$Y^{2+}(aq)$	$Z^{2+}(aq)$	$W^{2+}(aq)$
X(s)	X	X	X	✓
Y(s)	✓	X	✓	✓
Z(s)	✓	X	X	✓
W(s)	X	X	X	X

✓ spontaneous reaction
X no evidence of reaction

6. The strongest oxidizing agent is
A. $X^{2+}(aq)$
B. $Y^{2+}(aq)$
C. $Z^{2+}(aq)$
D. $W^{2+}(aq)$

7. The metal that has the weakest attraction for its electrons is
A. W(s)
B. Z(s)
C. Y(s)
D. X(s)

8. Which of the following solutions should *not* be stored in a tin-plated container?

I	$NaNO_3(aq)$	III	$SnBr_2(aq)$
II	$AgNO_3(aq)$	IV	$Cl_2(aq)$

A. I only
B. II and III
C. II and IV
D. III and IV

Use this information to answer questions 9 and 10.

Ozone is a strong oxidizing agent that will oxidize aqueous iodide ions in an acidic solution to iodate ions. The unbalanced redox reaction equation is

$$___O_3(g) + ___I^-(aq) \rightarrow ___IO_3^-(aq) + ___O_2(g)$$

9. When the half-reaction equations are constructed using coefficients to balance electrons, the number of electrons transferred is
A. 6
B. 3
C. 2
D. 1

10. NR The coefficients of the net redox equation, in the order of substances in the equation, are

___, ___, ___, and ___.

11. The oxidation number of the carbon atom in the carbonate ion is
A. +6
B. +4
C. –2
D. 0

Use this information to answer questions 12 to 14.

Many natural gas wells, called "sour" gas wells, contain considerable quantities of hydrogen sulfide gas as well as methane. When this mixture burns (**Figure 1**), hydrogen sulfide is converted to sulfur dioxide. Once in the atmosphere, sulfur dioxide may be converted to sulfur trioxide.

Figure 1
A flaring gas well

12. The oxidation numbers of the sulfur atoms in hydrogen sulfide, sulfur dioxide, and sulfur trioxide are, in order of these compounds,
A. 0, 0, 0
B. −2, +4, +6
C. −2, +4, +4
D. +2, −4, −6

13. In the two-step conversion from hydrogen sulfide to sulfur trioxide, the sulfur atoms are
A. oxidized in both steps
B. reduced in both steps
C. oxidized first, then reduced
D. reduced first, then oxidized

14. An unintended consequence of this process may be
A. depletion of the ozone layer
B. natural gas shortages
C. altering local climate
D. acid rain (deposition)

---

15. NR In a standardization experiment, 25.0 mL of an acidic 0.100 mol/L tin(II) chloride solution required an average volume of 12.7 mL of potassium dichromate solution for complete reaction. The amount concentration of the potassium dichromate solution is _____ mmol/L.

Part 2

16. Write a theoretical description of a redox reaction. Include the following terms in your answer: electrons, oxidation, reduction, oxidizing agent, and reducing agent.

17. Use a table of relative strengths of oxidizing and reducing agents, such as the one in Appendix I, to answer the following questions.
(a) How can you predict whether or not a combination of substances will react spontaneously?
(b) If a spontaneous redox reaction occurs, what kinds of evidence might be observed?

18. **Define** each of the following in terms of both electrons and oxidation numbers.
(a) oxidation
(b) reduction
(c) redox reaction

19. For each of the following, complete the half-reaction equation and classify as an oxidation or reduction.
(a) $HClO_2(aq) \rightarrow HClO(aq)$ (acidic)
(b) $Al(OH)_4^-(aq) \rightarrow Al(s)$ (basic)
(c) $Br^-(aq) \rightarrow BrO_4^-(aq)$ (acidic)
(d) $ClO^-(aq) \rightarrow Cl_2(g)$ (basic)

20. DE Various pairs of metals and metal ions were combined and the evidence interpreted, as shown below:
$2\,Ga(s) + 3\,Cd^{2+}(aq) \rightarrow 2\,Ga^{3+}(aq) + 3\,Cd(s)$
$Ga(s) + Mn^{2+}(aq) \rightarrow$ no evidence of reaction
$3\,Mn^{2+}(aq) + 2\,Ce(s) \rightarrow 3\,Mn(s) + 2\,Ce^{3+}(aq)$
(a) Use this information and the redox spontaneity rule to develop a table of oxidizing and reducing agents for these metals and their ions.
(b) **Identify** the strongest oxidizing and the strongest reducing agent in your table.

21. For the following solutions, list the entities believed to be present, and classify them as possible oxidizing or reducing agents.
(a) aqueous chlorine solution
(b) tin(II) nitrate solution
(c) acidic potassium iodate solution

22. For each of the following mixtures, list and classify the entities present, **predict** the half-reaction and net ionic reaction equations, and **predict** whether or not a spontaneous reaction will be observed.
(a) Chlorine gas is bubbled into an iron(II) sulfate solution.
(b) Nickel(II) nitrate solution is mixed with a tin(II) sulfate solution.
(c) A zinc coating on a drain pipe is exposed to air and water.
(d) An acidic solution of sodium sulfate is spilled on a steel laboratory stand. (Consider only the iron in the steel.)
(e) For use in a titration, a sodium hydroxide solution is added to a potassium sulfite solution to make it basic.

23. The reactivity of metals varies considerably from very low reactivity (noble metals) to explosively reactive. **Design** an experiment to study the reactivity of calcium metal in water. Your response should include:
- Purpose
- Problem
- Prediction, including half-reaction and net ionic equations
- Design, including diagnostic tests
- Materials, including WHMIS safety cautions
- Procedure, including disposal instructions

24. **Predict** the balanced redox reaction equation by constructing and labelling oxidation and reduction half-reaction equations.

(a) $Pt(s) + NO_3^-(aq) + Cl^-(aq) \rightarrow PtCl_6^{2-}(aq) + NO_2(g)$ (acidic)

(b) $CN^-(aq) + ClO_2^-(aq) \rightarrow CNO^-(aq) + Cl^-(aq)$ (basic)

(c) $PH_3(g) + CrO_4^{2-}(aq) \rightarrow Cr(OH)_4^-(aq) + P_4(s)$ (basic)

25. Assign oxidation numbers to all atoms/ions and indicate which atom/ion is oxidized and which is reduced.

(a) $2\,Al(s) + Fe_2O_3(s) \rightarrow 2\,Fe(s) + Al_2O_3(s)$

(b) $In(s) + 3\,Tl^+(aq) \rightarrow In^{3+}(aq) + 3\,Tl(s)$

(c) $2\,Cr^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2\,Cr^{2+}(aq) + Sn^{4+}(aq)$

(d) $Cl_2(aq) + 2\,I^-(aq) \rightarrow 2\,Cl^-(aq) + I_2(aq)$

(e) $UCl_4(s) + 2\,Ca(s) \rightarrow 2\,CaCl_2(s) + U(s)$

26. Balance the following chemical equations using the oxidation number method.

(a) $C_6H_{12}O_6(s) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$

(b) $Au^{3+}(aq) + SO_2(aq) \rightarrow SO_4^{2-}(aq) + Au(s)$ (acidic)

(c) $BrO_3^-(aq) + C_2H_6O(aq) \rightarrow CO_2(g) + Br^-(aq)$

(d) $Ag(s) + NO_3^-(aq) \rightarrow Ag^+(aq) + NO(g)$ (acidic)

(e) $HNO_3(aq) + SO_2(g) \rightarrow H_2SO_4(aq) + NO(g)$

(f) $Zn(s) + BrO_4^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + Br^-(aq)$ (basic)

27. Balanced redox equations can be obtained using three different methods, other than trial-and-error for simple equations.

(a) Briefly **describe** each method.

(b) Which method is also used to predict the products? What other information can also be predicted?

(c) For which methods do you need to know the primary products?

(d) Which method do you prefer to use? Why?

28. A commercial kit is available to clean silver by removing the tarnish using a redox reaction. (Assume that silver tarnish is silver sulfide.) A zinc strip is placed in a water softener solution and the tarnished silver is placed so that it is in contact with the zinc strip.

(a) Write the overall chemical equation and balance it using the simplest possible method.

(b) **Verify**, using oxidation numbers, that the chemical equation is balanced.

(c) Write oxidation and reduction half-reaction equations.

29. Magnesium metal reacts rapidly in hot water. **Predict** the mass of precipitate that will form if a 2.0 g strip of magnesium reacts completely with water.

30. A student uses a redox titration to determine the concentration of iron(II) ions in an acidic solution. The evidence in **Table 2** shows the volume of 7.50 mmol/L $MnO_4^-(aq)$ that reacted with 10.0 mL of $Fe^{2+}(aq)$. Calculate the amount concentration of the iron(II) ions.

Table 2 Titration of 10.0 mL of $Fe^{2+}(aq)$ with 7.50 mmol/L $MnO_4^-(aq)$

Trial	1	2	3
final burette reading (mL)	16.4	31.4	46.3
initial burette reading (mL)	1.3	16.4	31.4

31. Three chemistry teachers developed a problem to test students' understanding of redox concepts. The challenge is to identify three unknown solutions (labelled A, B, and C) using any of the materials listed below in your procedure. Assuming all possible spontaneous reactions are rapid and that the nitrate ion is a spectator ion, write a procedure to identify which solution is sodium nitrate, which is lead(II) nitrate, and which is calcium nitrate. **Describe** the expected results.

0.25 mol/L solutions of A, B, and C
silver, zinc, and magnesium strips
dropper bottles of 0.25 mol/L aqueous solutions of:
sodium sulfate; sodium carbonate; and sodium hydroxide
steel wool
test tubes and test tube rack
50 mL beakers
400 mL waste beaker

32. Photofinishing laboratories (**Figure 2**) often produce a waste solution containing silver ions. The CEO of a company wants to know if it is economical to recover this silver. The first step in the study is to determine the concentration of silver ions in the waste solution.

(a) Write an experimental design based on redox concepts to determine the concentration of silver ions.

(b) Using appropriate terms and chemical equations, **explain** the redox chemistry in your proposed design.

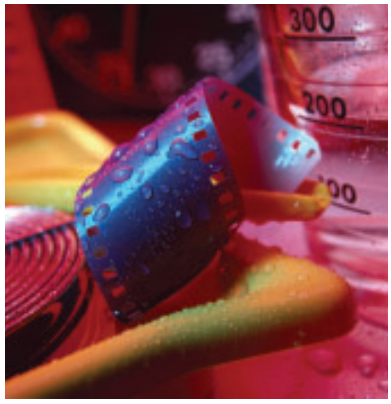

Figure 2
In film processing, the film is placed in a developing agent.

33. Methanol is used as a windshield-washer antifreeze; containers are usually labelled with the freezing point of the solution (**Figure 3**). A chemical technician can test the validity of the claim using various experimental designs. The experimental design chosen below is the titration of a basic solution of methanol with a standardized solution of potassium permanganate based on the following (unbalanced) chemical equation.

$CH_3OH(aq) + MnO_4^-(aq) \rightarrow CO_3^{2-}(aq) + MnO_4^{2-}(aq)$

Use the information in **Tables 3**, **4**, and **5** and complete the Analysis of the investigation report.

Purpose

The purpose of this investigation is to use redox stoichiometry for a chemical analysis.

Problem

What is the freezing point of a sample of windshield-washer fluid?

Design

A potassium permanganate solution is prepared and standardized against an acidic 0.331 mol/L solution of iron(II) ammonium sulfate (**Table 3**). The standardized permanganate solution is then titrated against a basic methanol solution, which has been diluted by a factor of 1000 (**Table 4**).

Evidence

Table 3 Titration of Potassium Permanganate Solution with 10.00 mL Acidic $FeSO_4 \cdot (NH_4)SO_4(aq)$

Trial	1	2	3	4
final burette reading (mL)	13.3	25.8	38.1	12.9
initial burette reading (mL)	0.2	13.3	25.8	0.5

Table 4 Titration of Standardized Potassium Permanganate Solution with 10.00 mL $CH_3OH(aq)$

Trial	1	2	3
final burette reading (mL)	12.4	24.1	35.8
initial burette reading (mL)	0.7	12.4	24.1

Table 5 Concentrations and Freezing Points of Aqueous Solutions of Methanol

Amount concentration (mol/L)	Percent by mass (%)	Freezing point (°C)
0	0	0
6.035	20.00	−15.0
11.672	40.00	−38.6
16.754	60.00	−74.5

Figure 3
This methanol windshield-washer antifreeze can be used at temperatures above −45 °C.

Extension

34. DE For the production of pulp from wood, a variety of methods are used, including mechanical and chemical processes. These have advantages and disadvantages that have been widely debated. Prepare an argument for or against the following statement: "The immediate economic value of using technology to produce a product far outweighs any possible future adverse effects."

Your response should also include

- researched information about a variety of mechanical and chemical processes
- an evaluation of these processes from technological, economic, and ecological perspectives
- reference to redox chemistry

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35. DE Vanadium (**Figure 4**) is a very versatile element in terms of its reactivity. Vanadium metal reacts with fluorine to form VF_5, with chlorine to form VCl_4, with bromine to form VBr_3, with iodine to form VI_2, with oxygen to form V_2O_5, and with hydrochloric acid to form VCl_2.

(a) **Identify** the oxidation states of vanadium in each of these compounds.

(b) What interpretation can be made about the oxidizing power of chemicals that react with vanadium metal?

(c) **Describe** how the oxidation state of vanadium relates to the colours of the compounds formed.

(d) Briefly **describe** some technological applications of vanadium and its compounds.

Figure 4
Vanadinite is the most common vanadium ore found in large reserves in many countries, including Canada.

36. The earliest metallurgy would be classified as pyrometallurgy. Other processes such as hydrometallurgy and electrometallurgy are more recent inventions. **Define** each of these types of metallurgy and provide one common example of each. Why are all three of these processes examples of redox reactions? What do these processes illustrate about the goal of technology and the interaction between science and technology?

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37. DE The nitrogen cycle (**Figure 5**) is a very important and complex biological system that includes nitrogen fixation, nitrification, and denitrification. **Describe** the chemical reactions in the nitrogen cycle.
Your response should include:

- definitions of the terms *nitrogen fixation, nitrification*, and *denitrification*.
- a summary of the main changes of nitrogen-containing entities and their oxidation numbers in the nitrogen cycle
- some examples of the half-reaction equations, labelled as oxidation or reduction
- descriptions of some positive and negative environmental impacts of the processes in the nitrogen cycle.

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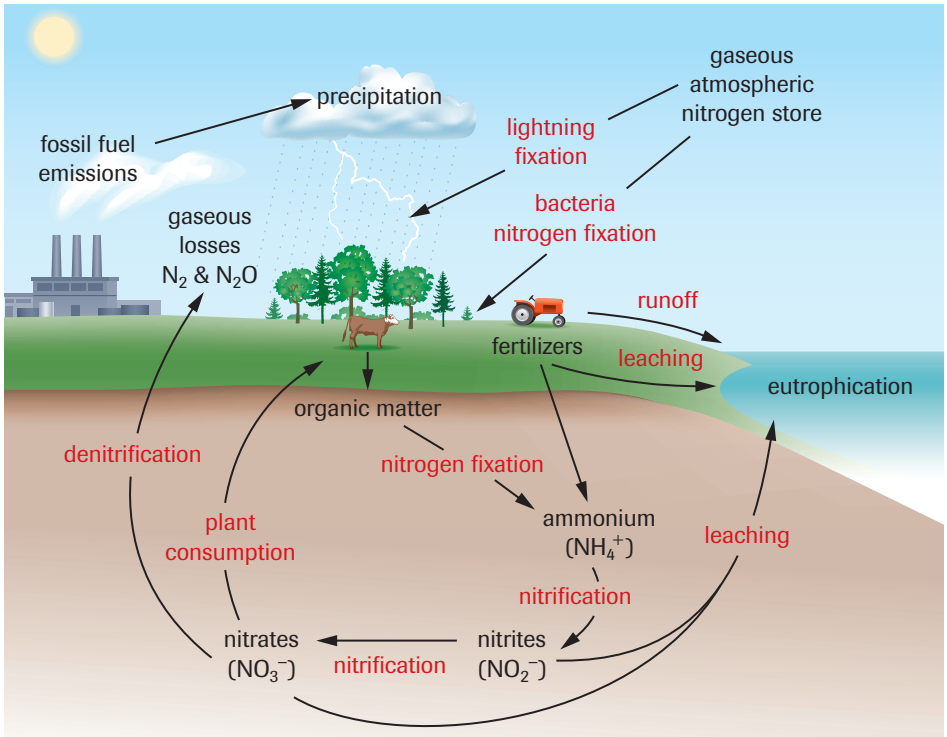

Figure 5
The nitrogen cycle